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INDUSTRIAL AND MANUFACTURING CHEMISTRY

VOL. I

ORGANIC

A PRACTICAL TREATISE

B 2619

BY

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PREFACE TO FIRST EDITION

THIS book is a treatise on the applications of Organic Chemistry to the arts and manufactures. It embraces both British and American practice, and affords, so far as is ascertainable in view of the many secret processes employed, thoroughly up-to-date information regarding the various branches of chemical industry and of manufactures having a chemical basis.

The editor's aim has been to cover the whole range of subjects with which the industrial chemist and manufacturer are usually concerned, and the book will serve either as a text-book or as a work of reference; it is intended to meet the requirements of all business and practical men interested in chemical processes, of manufacturers, consulting chemists, chemical engineers, patent workers, inventors, technical lawyers, students in technical institutions, lecturers on technology, fire insurance inspectors, and others.

Statistics, so important from a commercial standpoint, are made a feature of the work.

Particular pains have been taken to incorporate not only the main industries but also minor industries and new and out-of-the-way processes and products, the details of which are usually known to and obtainable by only a limited circle; moreover, these minor industries have potential importance as the germs of future great industries, and frequently, too, as affording, through absence of competition, profits far greater than those of fully developed trades. A striking example of this is afforded by artificial silk, which so took the market by storm (on account of its extreme brilliance) that for a time its price actually exceeded that of the real article.

The profitable utilisation of by-products—a matter of great importance to many manufacturers—has received special consideration.

Patent specifications are usually the first and often the only information appearing in regard to a technical process, and it is therefore unnecessary to apologise for the large number of recent

[redacted]its referred to in the text. Commercially many of them are [redacted]munerative, yet they often contain useful ideas.

[redacted]Matters calling for industrial research have been specially [redacted]phasised by the editor; for he has recognised that the subject [redacted] chemical industry is not only one which is full of problems [redacted]ose solution demands the highest technical skill, but also one [redacted]at holds out prizes of very great value to the scientific worker. [redacted]or example, great fortunes lie in the discovery of economical [redacted]rocesses for converting heavy mineral oil into light motor spirit, for [redacted]he synthetic production of rubber, or for the proper utilisation of [redacted]old leather for glue and gelatine manufacture; while the most far-reaching changes in the social and economic life of civilised nations have been made by the discovery of chemicals such as nitro-explosives, vulcanised rubber, synthetic dyes and drugs, technical alcohol, motor spirit, alkalis, glasses, metals, and artificial manures.

Much of the information in this volume is published in book form for the first time, and many of the descriptions of new processes and modern plant have been privately supplied through the courtesy of industrial chemists and of leading firms of Europe and America.

Full literary references are [redacted] the reader may have bef[redacted] prefixed to each article, so that all countries. Ind[redacted] account of li[redacted]ore him at once the main authorities of bran[redacted] Indeed, the editor ventures to think that the [redacted]literature relating to chemical technology in its organic [redacted]nches is the most complete ever published in English, and to hope that it will accordingly prove indispensable to the manufacturing or consulting chemist, the student, and the business man; for these often experience extreme difficulty in ascertaining where to find quickly some special piece of information lying outside the confines of the main industries.

The index has, therefore, been made as complete as possible, and numerous cross references are given.

The development of industrial chemistry, and the variety and comprehensiveness of its applications, has proceeded, during the past few years, at a rate so bewildering, and has taken such curious and unexpected turns, that the days are now past when one man, however well qualified, could keep abreast of recent advances in the different branches. Consequently, the editor has been fortunate in securing the co-operation of a number of experts as contributors on their special subjects: their names and attainments, enumerated on the title-page, and, more specifically, in

the List of Contents, are a guarantee that the minutest care has been exercised to ensure accurate descriptions of the industries concerned, and to these gentlemen the editor owes a considerable debt of gratitude.

It is impossible to thank in detail all those who have supplied information, or who have given help in subjects in which they have specialised. Nevertheless the editor cannot forego expressing his indebtedness to—Dr H. J. S. Sand, of Nottingham, for expert technical information; Dr G. Druce Lander, of London, for advice on certain technical problems; Mr C. Ainsworth Mitchell, B.A., F.I.C., for information on Vinegar Manufacture and for suggestions; Dr Newton Friend for help and advice in preparing many sections; Mr Geo. Stade, technical chemist. Berlin, for information on Continental molasses distilleries; Mr Geo. Clough, B.Sc., for material assistance in many ways; Mr J. Louis Foucar, B.Sc., for expert advice on the Coal-Gas and Coal-Tar Product Industry; Mr Dewar, F.I.C., for information on Linoleum Cements; Mr Paul Arup for information on Margarine; Mr Ernest Dancaster, B.Sc., for information on the Turpentine Substitutes and on the Graphitic and Grey Paints used by certain engineering companies; Mr J. B. Cotton for help.

Among other gentlemen who have helped are—Mr W. H. Stephens, A.R.C.S.; Mr A. J. Carrier, B.Sc.; Mr T. Beacall, B.A.; Mr G. M. Painter, B.Sc.; Mr Milsom, B.Sc.; Dr A. Slator; Mr J. W. Barker, A.R.C.S., B.Sc.; Mr F. Allen; Mr J. E. Mason; and Mr W. F. F. Shearcroft. Many of the great chemical firms have supplied full details of their more important patents, and even drawings of the plant used in carrying out certain of their manufactures. To all of these the editor returns his best thanks.

Although every care has been taken in the production of this work, yet, in view of the mass of detail involved, it is impossible that all errors have been eliminated, or that in every case the best processes have been described. The editor will therefore be grateful if industrial chemists, manufacturers, and other practical men will kindly inform him of any erroneous statements, or will call his attention to any serious omissions. Suggestions for increasing the utility of the work will be especially welcome.

PREFACE TO SECOND EDITION

THE fact that a new edition of a large book like the present one is called for in so short a time after publication indicates that it supplies an urgent want in technical literature.

In the present edition the various sections have been brought up to date, while fresh sections have been added on the new industry of the hydrogenation of fats, the manufacture of milk sugar, the manufacture of maize and arrowroot starch, the analysis of rubber, and the new synthetic tanning materials.

Mr F. B. Gatehouse, editor of the *Acetylene Lighting and Welding Journal*, has contributed the article on Acetylene, while Mr Gerald H. Martin has contributed the article on Rubber Analysis—a subject in which he has had an extensive experience.

In Appendix II. is given an index list of Trade Names of the newer Synthetic Drugs, Photographic Developers, etc., which will probably prove useful to many readers, as the information contained therein has hitherto proved difficult of access. The list originally appeared in the *Journal of the Society of Chemical Industry*, 1914, **33**, 1028, and is reproduced here with the Editor's kind permission.

In preparing this second edition for the press, much valuable help has been derived from readers, who have written to point out omissions or suggest improvements. The editor takes this opportunity of thanking these readers, and will be very pleased if practical men will inform him of errors or omissions which have escaped notice in spite of every effort to secure accuracy.

GEOFFREY MARTIN.

LONDON, *May* 1915.

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SECTION I

The Oil, Fat, Varnish, and Soap Industry

THE OIL, FAT, VARNISH, AND SOAP INDUSTRY

GENERAL NATURE OF OILS, FATS, AND WAXES

By C. Ainsworth Mitchell, B.A., F.I.C.

Nature of Oils.—The substances popularly known as "oils" fall naturally into the three groups—mineral, essential, and fatty oils.

To the first group belong the petroleum derivatives, consisting, in the main, of mixtures of various hydrocarbons, which, since they boil at different temperatures, may be separated by distillation into fractions such as naphtha, kerosene, heavy lubricating oils, and paraffin wax.

Essential oils, which constitute the second group, are volatile substances which occur in different parts of plants. For the most part they are mobile liquids, lighter than water, and as a rule are completely volatile without decomposition. Exceptionally, as in the case of oil of wintergreen which is fairly pure methyl salicylate, they do not consist mainly of a single compound, but usually they are composed of mixtures of various chemical compounds, such as hydrocarbons, aldehydes, and alcohols. The characteristic odour or flavour of an essential oil is usually centred in one or more of these constituents, and an estimation of the proportion of these substances affords a means of judging of the value of a given oil.

Fatty oils, which form the third group, are deposited in the adipose tissue of animals, or in the oil cells of seeds or other parts of plants, occurring in the form of minute globules enclosed within a thin skin. Chemically, they consist of compounds of an alcohol such as glycerol with one or more fatty acids. In these glycerides the three bonds of the glycerol may be in combination with the same fatty acids (*e.g.*, tristearin); or two bonds may be in combination with one fatty acid and the third with another one (*e.g.*, dipalmitostearin); or all three bonds may be combined with different fatty acids (*e.g.*, oleo-palmito-stearin). Mixed glycerides of the two latter types have been discovered in natural fats.

The properties of the fatty acids isolated from fats by means of saponification afford valuable analytical evidence of the nature of the oils whence they are derived.

Waxes differ from fats, properly so-called, in having the fatty acids combined with an alcohol other than glycerol. Thus sperm oil, regarded from a chemical point of view, is as much a wax as the typical product, beeswax; whereas Japan wax, so-called from its wax-like appearance, is in reality not a wax at all, but a true glyceride.

I.—MINERAL OILS AND LUBRICANTS, INCLUDING THEIR CHEMICAL EXAMINATION

By C. Ainsworth Mitchell, B.A., F.I.C.

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Manufacturing Processes.—Crude petroleum, which is probably a product of the decomposition of animal or vegetable remains, is found deposited in oil-bearing strata in various parts of the globe or in a partially oxidised condition upon the surface, whither it has found its way through fissures in the rocks.

It is now usually obtained by Drake's method of sinking the drill through a hollow tube, in some instances to a depth of 2,000 to 3,000 ft.; and in the case of the larger oil-fields is conveyed by a system of pipe lines to the refineries, which are situated near the points of distribution.

In Scotland a considerable quantity of oil is obtained by distilling certain bituminous shales. The product is known as "shale oil" and is otherwise pumped and distilled much in the same way as crude petroleum oils.

The bituminous shales may be regarded as intermediate in character between natural asphalt and the oil-bearing rocks whence petroleum is obtained, and probably represent the residues of fish and other fossil marine organisms. As in the distillation of coal, large amounts of ammonium sulphate are obtained. For statistics, see p. 13.

The mineral oils are composed principally of saturated hydrocarbons.

American petroleum consists essentially of saturated paraffins, C_nH_{2n+2}, of which Methane, CH_4 (in natural gas), Pentane, C_5H_{12}, and Hexane, C_6H_{12} (in benzine), $C_{13}H_{28}$ (B.P. 225° C.), $C_{18}H_{88}$ (B.P. 300° C.) (in light petroleum).

Russian petroleum consists essentially of a number of hydrocarbons of the naphthene series C_nH_{2n}, such as, *e.g.*, Heptanaphthene, C_7H_{14} (B.P. 100° C.);

Pentadekanaphthene, $C_{15}H_{30}$ (B.P. 247° C.), etc. These are cyclic polymethylenes, and differ from unsaturated olefines of the same formula in that they do not form addition compounds with bromine, and are only slightly attacked by HNO_3 and H_2SO_4.

The higher boiling fractions of all crude mineral oils consist largely of unsaturated hydrocarbons, *e.g.*, olefines, C_nH_{2n}, acetylenes, C_nH_{2n-2}, and other still more unsaturated bodies. It is the presence of these higher boiling unsaturated hydrocarbons which makes crude oil on standing polymerise and oxidise, becoming yellow and ultimately being converted into resinous-like substances (*e.g.*, natural asphalts). It is remarkable that in these mineral oils only traces of benzene hydrocarbons, C_6H_6, $C_6H_5CH_3$, etc., occur; also Russian petroleum usually contains no solid paraffin, while considerable amounts are found in American and Galician oils. A small amount of oxygen—sometimes 2 per cent.—is present, owing to the presence of organic acids and phenols. A small amount of N is also usually present. Some mineral oils, however, contain considerable amounts, *e.g.*, Californian oil contains 2 per cent. N = 15 per cent. nitrogenous matter. The presence of S (in the form of organic sulphides) is particularly harmful and makes refining difficult. Some Californian oils contain 2 per cent. S, and in consequence of their unpleasant odour can only be used as fuel or for lubricating purposes.

The process of refining employed largely depends upon the composition of the *oil* and the uses for which it is intended. Where a large yield of lamp oils is desired from the crude petroleum the "Cracking process" is employed. In this the oil is first distilled until products of the naphtha and rol class have passed over, er which the temperature is sed, and the bulk of lamp oils lected in another receiver. e next portion of the distillate ow made to fall back into the , which has meanwhile been ted to a higher temperature, this causes decomposition of oil intermediate in type to e of the illuminating and icating class. The distillan is then continued until a ry residue is left in the still, nd this residue is subsequently nited with similar residues, and distilled again, so as to obtain fractions of heavy oils, paraffin wax, and a final residue of tar and coke.

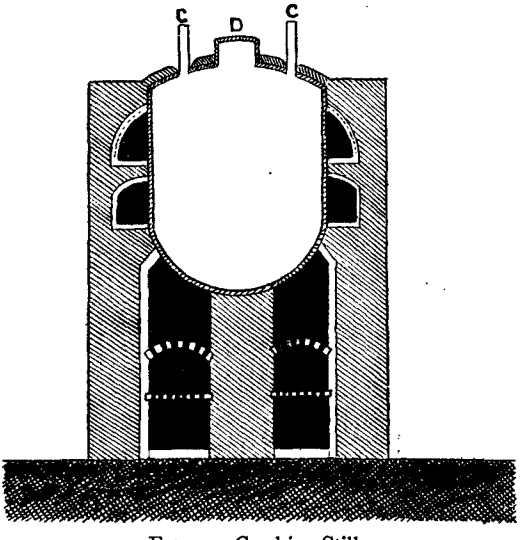

FIG. 1.—Cracking Still.

Fig. 1 shows a cast-iron cracking still with hemispherical bottom employed in Russia. After the more volatile products have been distilled off, the heat is carefully regulated by dampers, and a suitable dephlegmator is used to return the heavier oils carried over during distillation, the oils dropping back into the still and being there decomposed into lighter constituents.

When distillation is carried to dryness the residual coke is removed through the manhole D. Very often the distillation is aided by the introduction of steam.

Fig. 3 shows a Russian still. A is the still; B the still head; C C the condensing pipe; D a collecting vessel, whence the oils run into reservoirs. The more volatile portions are condensed by a coil E surrounded by cold water. Steam is driven in through *a* or *b*. The vacuum process of distillation is very general for lubricating oils. Fig. 4, p. 10, shows a still used for this purpose. The lighter boiling portions are rectified in special stills similar to those employed in the manufacture of industrial alcohol; for these see Fig. 2, p. 6, and pp. 297-311.

The rise into importance of the motor car industry has caused a great demand for the more volatile constituents of petroleum. Consequently several new "cracking" processes have been employed to increase the yield of those lighter constituents at the expense of the heavier lubricating and illuminating oils.

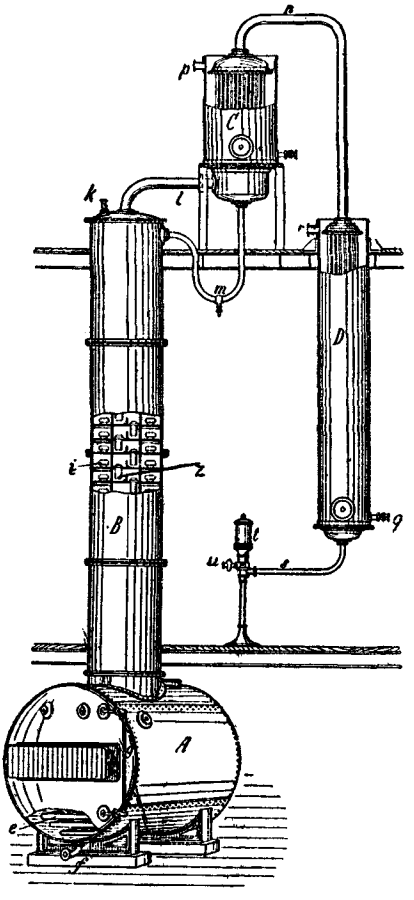

FIG. 2.—Still, with Column, for Fractionating Light Petroleum.

Thus Cowper-Coles (English Patent, 27,945, 1906) distils paraffin and passes the vapours through a series of small metal tubes heated to a temperature sufficiently high to decompose partially the vapour, which is then conducted into a condensing apparatus so as to condense it. The liquid thus obtained has a much lower flash-point than the petroleum originally placed in the tube. Thus Coles states that if the original flash-point is 120° F., the flash-point of the resulting liquid may be as low as 16° F.

Noad and Townsend (English Patent, 13,675, 1908) pass a mixture of petroleum and water into a hot air-free chamber filled with red-hot scrap iron, which acts as a catalytic agent. The products react, and on condensing the vapours and separating the oil and water by fractional distillation a petroleum is isolated having a much lower flash-point than the original petroleum. Noad and Townsend state that practically the whole of the oil is converted into volatile spirit, only a very small percentage of residual carbon and permanent gas being obtained.

When more lubricating oil is required the "cracking" process is omitted, the receivers changed at an earlier period. In another process continuous distillation is employed, the oil being passed from still to still, each of which is heated to a higher temperature.

The crude oil is invariably separated by this distillation into three fractions: (1) Crude benzine, B.P. up to 150° C., sp. gr. 0.75-0.77, called benzine or petroleum naphtha; (2) Kerosene, B.P. 150°-300°; sp. gr. 0.87 (illuminating oil); (3) Residuum in still, boiling above 300° C.

After distillation, the fractions are purified by redistillation to remove traces of impurities, and by a chemical treatment with concentrated sulphuric acid (which removes unsaturated hydrocarbons and bases), followed by caustic alkali (to remove acid bodies) and sometimes litharge (to remove all traces of sulphur) or copper oxide. For certain purposes it is also necessary to bleach and filter the oils. Finally the paraffin wax which separates is freed as completely as possible from water and then expressed in a hydraulic press at a low temperature to expel the oil.

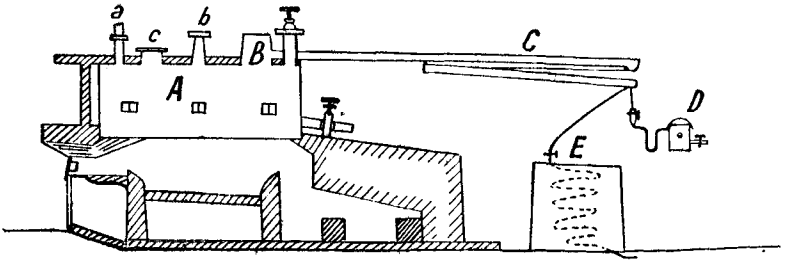

FIG. 3.—Russian Petroleum Still.

The proportions of these various products obtainable from a given crude petroleum oil depend upon the composition of the original substance as well as upon its treatment.

The following typical analyses show the yields that may be expected :—

Crude Petroleum Oils.	Naphthas.	Illuminating Oils.	Lubricating Oils.	Paraffin Wax.	Tar.	Coke.	Loss, etc.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Burmese (sp. gr. 0.885) -	...	39.8	41.8	6.2	4.5	...	7.7 (including gas)
Pennsylvanian (sp. gr. 0.802)	14.5	39.5	38.6	2.4	...	2.0	3.1
,, (sp. gr. 0.870)	5.3	41.8	46.6	3.1	...	2.4	0.8
Canadian (sp. gr. 0.823) -	11.7	36.4	44.5	2.8	...	3.0	1.6

It is usual to group under the name of "naphthas" the fractions boiling below 150° C. Between that temperature and 300° C. come the illuminating or lamp oils (kerosenes); while the fractions distilling above 300° C. form the lubricating oils.

The naphthas are further graded by refining and redistillation into fractions, such as *gasoline* (sp. gr. 0.655); *naphtha* or *benzoline* (sp. gr. 0.705); and benzine (sp. gr. 0.737).

The following results quoted by Allen ("Comm. Org. Anal.," III. 106) show the yields of the respective products obtainable from typical American petroleum and from Scotch shale oil :—

Products.	Petroleum Oil.		Shale Oil.	
	Sp. gr.	Per cent.	Sp. gr.	Per cent.
Cymogene and rhigolene -	0.590-0.625	Very small	...	Very small
Gasoline - - - -	0.636-0.657	1.0-1.5		
"C" naphtha - - -	0.700	10	0.730	5
"B" naphtha - - -	0.714-0.718	2.5		
"A" naphtha (benzine) -	0.725-0.737	2.0-2.5		
Kerosene - - - -	0.802	50-55	0.800-0.810	37
Lubricating oils - -	0.875	17.5	...	17
Paraffin wax - - -	...	2.0	...	13
Coke, gas, and loss - -	...	8-10	...	28

Russian petroleum oil being distilled by the continuous process, in which both dry heat and superheated steam are used for heating the stills, gives very different yields of the various products. The usual amount of tar obtained is upwards of 20 per cent., and no paraffin wax is separated. The lubricating oils derived from Russian petroleum are of a darker colour, and more viscous than those of American and Scotch origin, but they become fluid more readily when heated. They also give off inflammable vapour at a lower temperature than the other oils of corresponding specific gravity. Owing to the fact that they can be exposed to a low temperature without throwing down a deposit they form the better lubricants for cold climates.

Benzine, Petroleum Naphtha, Petroleum Spirit

Those portions of Pennsylvanian oils which boil under 150° first became important when they began to be used for the dry cleaning of clothes (since 1860). Later, benzine was used on a very large scale for extracting fat from cocoa-nuts and bones in place of the dangerous carbon bisulphide. Within recent years an enormous demand of the more volatile constituents of petroleum ("motor spirit") has been set up by the development of the motor car industry, and at the present time these portions exceed in price the higher boiling "illuminating oils."

American benzines have a sp. gr. about 0.02 *less* than that of Russian benzines of the same boiling point. The former consist essentially of paraffins, and the latter of cyclic-polymethylenes. Before use the crude benzine must be carefully purified by treating with concentrated H_2SO_4 and NaOH, and then fractionated in column apparatus (see under **Spirit Distillation**, p. 295, *et seq.*).

For this purpose the oil is allowed to flow in succession through a series of iron cylinders, entering at the bottom and flowing out near the top; the first of these cylinders is lead-lined and contains concentrated (66 per cent.) H_2SO_4; the next one is empty (so that the concentrated H_2SO_4 deposits) and the succeeding ones are filled with the caustic soda solution. The oil ultimately runs from there into an iron still furnished with a column apparatus (see p. 6) and heated with steam (a naked fire is too dangerous with volatile oil), and the oil carefully fractionated.

The following fractions are obtained from American naphtha :—

a. **Petroleum Ether, Gasoline, Solene,** B.P. 40°-70° C.; sp. gr. 0.64-0.65; consisting essentially of Pentane, C_5H_{12}, and Hexane, C_6H_{14}.

b. **Benzine,** B.P. 70°-120° C.; sp. gr. 0.70-0.72; sometimes further divided into lower and higher boiling fractions ("benzoline" and "naphtha" respectively). The benzoline and naphtha are both sold under the name of petroleum spirit, and also as benzine. They are colourless volatile liquids, possessing a peculiar odour, and entirely evaporating away on exposure to air without leaving a residue. They give off inflammable vapours at ordinary temperatures, and are consequently much used as "motor spirit," also for the "dry cleaning" of clothes and for extracting fat from bones and cocoa-nuts.

c. **Ligroin,** heavy benzine, B.P. 120°-135° C.; sp. gr. 0.73; and **Polishing Oil,** B.P. 130°-160° C.; sp. gr. 0.74-0.77, are sometimes used as a polishing oil for machinery, but also as turpentine substitutes in making varnishes and paints. These are rather slower in drying, but less inflammable than petroleum spirit.

Shale Spirit is obtained from Scotch shale. When this is distilled at a low temperature a quantity of tarry matter is obtained in the receiver. This is known as "crude oil," and is submitted to redistillation when "once-run oil" is obtained. The latter is washed with sulphuric acid, and then with caustic soda, and submitted to fractional distillation. The three chief distillates are known as "green naphtha," "twice-run light oil," and "green-oil." The "green naphtha" is washed with sulphuric acid, and then with caustic soda, and again distilled, when "shale spirit," also known as "shale naphtha," is obtained. Shale spirit is a very volatile, colourless liquid of sp. gr. 0.730-0.760. It possesses a slight odour, and is very inflammable, taking fire at ordinary temperatures. On exposure to the air it evaporates away without leaving any residue. Shale spirit contains a mixture of hydrocarbons, chiefly paraffins and olefines, the latter forming about 60 per cent. of the spirit. The heavier and higher boiling portions of the distillate are used as illuminating and lubricating oils. It is largely used as a substitute for turpentine, and is perhaps the next best to rosin spirit for this purpose.

Coal-Tar Naphtha, Benzene or Benzol, C_6H_6, is quite a different product from benzine or petroleum naphtha, being obtained by distilling *coal-tar* (see p. 416). It is similarly used as motor spirit, also for extracting fat and cleaning clothes, but it burns with a smoky flame, and so is not such a good motor spirit as petroleum benzine.

The Dry Cleaning of Clothes as practised in laundries is especially useful for woollen garments. It consists in (1) agitating the cloth in closed vessels with benzine, which dissolves out fat and the attached dirt; (2) rinsing with benzine; (3) "centrifuging" to get rid of the benzine and dry the cloth. The continual friction of the moving benzine in large extracting apparatus often causes it to become so highly charged electrically that it sparks and spontaneously inflames. Many explosions have occurred this way and precautions are always taken to detect a high degree of electrification of the moving oil. Magnesium oleate is sometimes dissolved in it to make it a better conductor of electricity and so diminish the danger of electrical sparking.

Carbon tetrachloride (see p. 31), chlorhydrine, and ethylene chlorides are also used for this purpose, and, though their vapours are poisonous, have the advantage of non-inflammability. These non-inflammable solvents are now fairly generally used in laundries.

Kerosene, Illuminating or Lamp Oils

This is the portion of the distillate boiling between 150°-300° C.

The chemical purification of American Pennsylvanian oil is much the same as that described under benzine, viz., first with concentrated H_2SO_4, and then with NaOH. The NaOH removes the petrolic acids as sodium salts, which are sometimes used as soap. Usually 0.5-1 per cent. of 66 per cent. H_2SO_4 is thoroughly stirred up with the oil by means of a stream of compressed air, and the tarry products allowed to settle and run off at the bottom. Next, the oil is similarly agitated with water, which is run off, then with NaOH solution, and finally with water. Sometimes it is further bleached by exposure to sunlight. It is imported as an almost colourless, weakly bluish-fluorescent liquid of sp. gr. at 15° C. = 0.803, containing about 85-86 per cent. C, and 13.5-14 per cent. H. There are, however, several varieties, having both higher and lower specific gravities than this.

Much of the present-day American illuminating oil comes from California, and the refining is especially difficult on account of the large amounts of sulphur it contains. Treating with PbO, leading the vapours over CuO (which is "regenerated"), and other methods of fixing the sulphur are employed, after which follows treatment with concentrated H_2SO_4 and NaOH.

The Russian Baku oils ("kerosene") are purified like the American Pennsylvanian. They have specific gravities varying from 0.809-0.8265 (15° C.) and possess a high illuminating power.

A considerable quantity of oil is also made for "carburetting" coal or water gas (see p. 397). Benzol is also used for the purpose (see p. 398).

Examination of Petroleum and its Products.—The methods of examining crude petroleum oil are based upon a fractional distillation upon a small scale, measuring the amounts of the various fractions obtained, and determining their physical properties, including the specific gravity, flash-point, viscosity, etc.

Specific Gravity.—Special hydrometers are constructed for rapidly testing the specific gravity of petroleum products, and for commercial purposes these are usually sufficiently accurate. For scientific purposes, however, greater accuracy is required, and the specific gravity should be determined with the aid of a specific gravity bottle or Sprengel's tube.

In the American trade, oils are usually described by their specific gravities, as for example "875 pale oil"; "885 pale oil"; "903-907 pale oil"; "910-912 pale oil."

Flash-point.—The temperature at which an oil gives off inflammable vapour is of the greatest importance in the case of illuminating and lubricating oils. A few years ago lamp oils were frequently sold with too low a flash-point, and were the cause of innumerable accidents, but this is now less common, since the greater demand for petrol has made it commercially profitable to remove more completely the portions boiling at a lower temperature.

The flash-point may be approximately ascertained by the "open test," which consists in heating a little of the oil in a porcelain crucible embedded in sand, and applying a light from time to time until the vapours take fire, the temperature being then read on a thermometer previously placed in the oil. For illuminating oils special apparatus is used, and this value is determined by the "close" method. In this country Abel's apparatus is used officially, while on the Continent Pensky's modification is usually the standard instrument. The results obtained by the two methods differ slightly, those given by Pensky's apparatus being, on the average, about 2° C. lower.

In America the "fire test," or the temperature at which the body of the oil takes fire, is also frequently made; but as Allen pointed out, this test gives erroneous results, since a kerosene oil, when spilled, may ignite at a temperature far below that shown by the test.

Speaking generally, an oil which flashes at about 73° F. in Abel's apparatus (or about 100° F. in the open test) would show a "fire test" of about 120° F.

Petroleum burning oils have a flash-point of 73°-110° F.; paraffin burning oils, 100°-120° F.; naphtha, 60°-70° F.; *linseed*, about 470° F; rosin, 310°-320° C.

Viscosity.—Various methods have been devised for obtaining some measure of the degree of the so-called "viscosity" of oils, but that generally employed consists in determining the time taken by a given quantity of oil to run through a small opening under definite conditions of temperature, etc.

For this purpose special apparatus is usually employed, the separate parts of which are made to standard measurements, so that results obtained by different workers may be comparable. The time in seconds (*i.e.*, the efflux velocity) may be compared with rape oil (or sometimes with water) as a standard substance, and the values obtained at different temperatures afford an indication of the probable behaviour of the oil when used as a lubricant.

The following figures given by Redwood * are typical of those obtained with a viscosimeter. The results are comparable among themselves, but are not reduced to a standard.

Oil.	Relative Time in Seconds (Redwood).						
	50° F.	70° F.	100° F.	140° F.	200° F.	250° F.	300° F.
Refined rape oil	712.5	405	147	105.5	58.5	43.25	...
Beef tallow	...	...	...	...	54.75	40	...
Sperm oil	...	136.8	60.5	50.75	42	34.75	30
Neatsfoot oil	620	366	126	88.4	50.4	44	38
American mineral oil (sp. gr. 0.885)	145	90	47	41	...	...	...
,, ,, (sp. gr. 0.923)	1,030	485	126	82	42	...	...
Russian ,, (sp. gr. 0.909)	2,040	820	174	116	48.5	...	...
,, ,, semi-solid	...	...	531	317.5	99.25	59.25	42.6

Calorific Power.—A determination of the calorific power of oils is valuable in the case of products intended for fuel or oil engines. It is usually estimated by combustion of the oil in oxygen in a calorimetric bomb; but it has been shown by Sherman and Kropff † that in the case of American oils, at all events, there is an approximate relationship between the calorific power and the specific gravity, which may be expressed by a formula.

Thus they have found the following values to correspond approximately :—

A sp. gr. of	0.7-0.75	indicates about	11,700-11,350 calories.
,,	0.75-0.08	,,	11,350-11,100 ,,
,,	0.8-0.85	,,	11,100-10,875 ,,
,,	0.85-0.9	,,	10,875-10,675 ,,
,,	0.9-0.95	,,	10,675-10,500 ,,

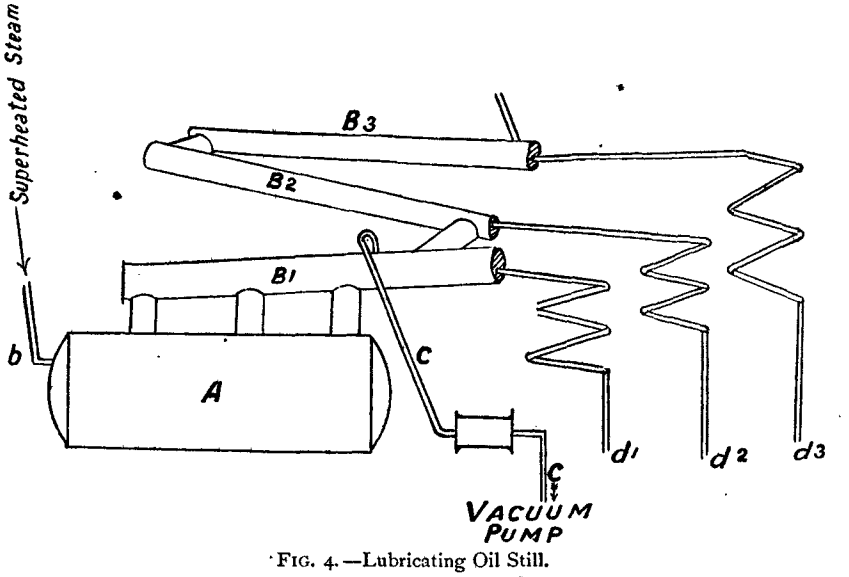

FIG. 4.—Lubricating Oil Still.

Still Residuum.—Lubricating Oils—Vaseline

The residue which remains in the stills after the oil boiling below 300° C. has been distilled over consists of 10-25 per cent. of Pennsylvanian oil, 50 per cent.

* Quoted by kind permission of Messrs Griffin & Co. from Redwood's "Petroleum."

† *Journ. Amer. Chem. Soc.*, 1908, 30, 1626.

Californian oil, and about 60 per cent. of the Baku oil. This residue is largely used as fuel ("Masut," "Oil Fuel"), but is also worked for *lubricating oils* and pitch by further distillation. The thinner portions of the distillate are used as "oil gas" for carburetting illuminating gas, while the thicker portions constitute the mineral lubricating oils. Some of the American and Galician residues are very rich in paraffin and are worked for this.

For the machine lubricating oils the residues are distilled in a vacuum with superheated steam, whereby decomposition is avoided, and to remove solid paraffins the oils are cooled and forced through a filter press. They are then treated with concentrated H_2SO_4, NaOH, and H_2O.

Fig. 4 is a rough diagram of a lubricating oil still. The petroleum still residues are placed in boiler A, superheated steam is driven in through b, while a high vacuum is maintained by means of the tube cc. The oil distils and passes up the dephlegmating tubes, B_1, B_2, B_3, and is there fractionally cooled, the least volatile oil running out through the condenser d_1, while a more volatile oil is collected from d_2, and the most volatile oil of all through d_3.

For coarse lubricating greases for rollers, wheel axles, etc., distillation is not resorted to, but a careful chemical purification with H_2SO_4 and NaOH (to remove pitch) is performed on the crude still residues.

Lubrication.—The choice of a lubricant depends principally upon the type of machinery for which it is required. Owing to the growth of the mineral oil industry the amount of fatty oils now used for this purpose is small in comparison with the former consumption, but for certain purposes fatty lubricants are still widely employed, either alone or in admixture with mineral oils.

Thus, for the wheels of clocks and other fine machinery, neatsfoot oil, hazel-nut oil, and lard oil are in common use, while inferior grades of olive oil, castor oil, rape oil, sperm and arctic sperm, and certain blubber oils, are also employed for cold machinery.

As is shown in the table on p. 10, the viscosity of fatty oil diminishes much more rapidly than that of mineral oils on raising the temperature, and it is therefore advantageous, where other conditions permit, to use a mixture of the two kinds of oil.

Oils belonging to the semi-drying class (*e.g.*, cotton-seed oil), or drying oils, such as linseed oil, are quite unsuitable as lubricants, owing to their rapidly absorbing oxygen from the air and becoming sticky. Oils of this class should not contain free mineral acid or more than a trace of free fatty acids, which gradually corrode metallic surfaces.

The objection to the use of fatty lubricating oils in cylinders or other machinery working at a high temperature is that the oil is partially decomposed, and that the iron is attacked by the liberated fatty acids.

Mineral Lubricating Oils.—As was mentioned above, in addition to the oils separated by distillation from crude petroleum as described, and having a sp. gr. of 0.840 and upwards, similar oils are prepared by the destructive distillation of lignite and shale, and redistillation of the residuum.

Certain oils of high density are obtained by the process of "sunning" or evaporation, by exposing the oil to the air or by concentrating it with steam at a low temperature, but the bulk of such oils is obtained by distillation.

Mixed oils, consisting of suitable proportions of fatty and mineral oils, are found in many lubricants on the market. The proportion of the former may be ascertained by determining the saponification value of the mixture.

Lubricating Greases.—These may contain solid fats, vaseline, various metallic soaps (especially those of aluminium) of fatty or resin acids, incorporated

with more liquid mineral or fatty oils or rosin oil, and sometimes blended with solid substances, such as plumbago. Products containing so many possible constituents must necessarily show considerable variations in composition, and the results of mechanical and physical tests, coupled with the absence of injurious substances, afford the best criteria of their suitability for lubricating purposes.

Water soluble oils are becoming more and more widely used owing to the presence of *alkali soap*. They readily emulsify with water, and are used to oil wool for spinning, to grease textile machines, for ointments, etc. Boleg (see German Patents, 129,480, 122,451, 148,168) makes heavy tar oils soluble in water by adding crude resin oils (which see), saponifying them with alkali, and oxidising under pressure. They will bear mixing with a considerable amount of water without becoming turbid.

Acheson's Deflocculated Graphite ("Dag"), recently put on the market, is obtained by macerating graphite with a solution of tannin or other organic fluid for several weeks, whereby it is so finely divided that it forms a permanent emulsion, containing 0.3 per cent. carbon, with water. This "molecular" graphite forms an excellent lubricant, 1 cubic inch of the graphite being equivalent to 5 gallons of oil. **Aqua-dag** is the graphite prepared with water. It prevents the rusting of iron, and has been employed with success in lubricating tools for cutting pieces of shafting. **Aqua-dag** is made by mixing the molecular graphite with water in barrels, allowing to stand three weeks, decanting, and passing through filter presses containing special cloth. The emulsion will not mix with oil. **Oil-dag** is prepared by pouring oil over the filtered dag, then pouring off the oil with some water. The dag is then treated in a vacuum to remove the water, and oil finally added. Both oil-dag and water-dag are largely used, although oil-dag has the advantage over water-dag that the oil does not evaporate (see *Engineering*, 17th November 1911, p. 673).

Examination of Lubricating Oils.—The flash-point of lubricating oils should be ascertained to show that the oil does not give off dangerous vapours at a low temperature. It should not be lower than about 175° C. in the open test, and about 100° C. higher than this for oils intended for use in cylinders.

Cold Test.—This is made by immersing the tube containing the oil in a freezing mixture and slowly stirring the contents until solid matter separates. The test is of great value in the case of oils which are intended to be used in cold climates, since an oil with high freezing point is liable to congeal in the machinery. In Prussia the State Railway specifies that an oil when examined in a special apparatus shall not solidify at −15° C. in winter or at −5° C. in summer, different classes of oil being thus permitted at different seasons.

Ash.—The amount of residue left on igniting a pure mineral lubricating oil is insignificant, whereas oils containing soaps of sodium, potassium, calcium, or aluminium will leave a material quantity of ash.

Water.—The presence of water in a mineral oil is indicated by a turbidity which causes the liquid to froth up when heated, whereas turbidity due to paraffin wax may be removed by heat.

Gumming Tendency.—The liability to "gum" or become sticky upon machinery may be roughly estimated by placing drops of equal size of different oils upon an inclined surface, and noting the time before the oil ceases to run, owing to its increased viscidity through oxidation. In addition to oils of the drying and semi-drying class (such as linseed and cotton-seed oils), resin oils and fish oils also absorb oxygen rapidly from the air, and become "thick." Hence they should not be used for lubricating purposes. Various chemical methods based upon a measurement of the amount of oxygen absorbed by an oil in a given time have also been devised.

Evaporation Test.—A weighed quantity of the oil is heated for a definite time at a constant temperature, and the loss in weight determined. In the case of oils intended for ordinary machinery, the temperatures of 60°-100° C. are employed, whereas for cylinder oil a temperature of 150°-300° C. is needed. According to Lant Carpenter a mineral oil losing more than 5 per cent. of its weight at 60° C. is unsuitable for lubrication, as it is liable to form a viscous residue and leave the bearings dry. In the case of cylinder oils the loss at 188° C. should not exceed 0.25-0.5 per cent. (Archbutt).

Tar and Coke.—In order to obtain further information as to the probable behaviour of lubricating oils at high temperatures, Kissling * has devised conventional methods of estimating the amounts of tar-like and coke-like substances present in an oil, and also the amounts formed after exposing the oil for fifty hours to a temperature of 150° C. In the estimations, the oil is heated with alcoholic alkali, and the aqueous alkaline extract subsequently extracted with benzene to separate tarry matters or treated with petroleum spirit to separate coke-like substances. The empirical values thus obtained are termed the "tar value" and the "coke value," and the corresponding "tar-forming" and "coke-forming" values may be found by similar estimations upon the heated oil.

* *Chem. Zeit.*, 1908, 32, 938.

The following results are typical of those given by different kinds of oil :—

	I. Before Heating.		II. After Heating for Fifty Hours at 150° C.		Total of I.	Total of II.
	Tar Value.	Coke Value.	Tar Value.	Coke Value.		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Steam cylinder oil, Pennsylvanian	0.023	...	0.185	0.020	0.023	0.205
Spindle oil, Pennsylvanian - -	0.090	...	0.299	0.114	0.090	0.413
Machine oil, German - - -	0.227	...	0.740	0.827	0.227	1.567
Turbine oil (used), Pennsylvanian	1.083	trace	1.463	1.199	1.083	2.662
Cylinder oil, Texas - - -	1.113	...	1.377	1.294	1.113	2.671
Heavy engine oil, Texas - -	1.234	...	1.220	1.128	1.234	2.348
Cylinder oil, Russian - - -	0.266	...	0.501	0.484	0.266	0.985
Heavy machine oil, Russian -	0.239	...	0.458	0.782	0.239	1.240
Spindle oil, Russian - - -	0.213	...	0.474	0.753	0.213	1.227

From the results of these tests Russian lubricating oils appear to be inferior, as regards the amount of tar they contain (or formed on heating), to Pennsylvanian oils, but better than Texas oils.

Vaseline is manufactured by carefully distilling suitable kinds of crude petroleum in vacuum stills (to diminish dissociation), and filtering the residue through animal charcoal filters heated to about 50° C. The first runnings are colourless and form **Vaseline**, the later runnings are brown and form "filtered cylinder oil."

Vaseline is manufactured from **Galician** oils (*a*) by evaporating the oils up to 340°, dissolving the syrupy residues in petroleum ether (sp. gr. 0.66), decolourising repeatedly with animal charcoal, and evaporating off the solvent; (*b*) by bleaching the crude oil by passing through steam-jacketed charcoal filters, and distilling in vacuo (10 to 15 mm.) at 250° C.

Vaseline consists of a mixture of hydrocarbons, and has the composition C = 86-87 per cent., H = 13-14 per cent.

Most of the "Vaselines" now on the market are merely artificial mixtures of ceresine (18 per cent.) with oils, sometimes (in poor qualities) with the addition of paraffin wax.

For **Rosin Oils** see p. 339.

Statistics.—The following figures show the quantity of mineral oil and vaseline imported into the United Kingdom :—

		1906.	1910.	Value in 1910.
Petroleum—				£
Crude	Galls.	1,112,710	187,318	3,310
Lamp oils	,,	151,239,979	138,828,483	1,850,918
Motor spirit	,,	26,792,687	*55,049,210*	*1,340,551*
Spirit, other than motor spirit	,,		239,948	4,872
Lubricating oils	,,	49,704,819	58,560,651	1,705,866
Gas oil	,,	56,551,321	57,507,131	477,704
Fuel oil	,,	13,819,091	34,363,276	262,455
Other sorts	,,	...	733,819	17,206
Vaseline and Mineral Jelly	Cwt.	...	21,773	47,960

The United States in 1910 *imported* 13,693,000 gallons (value, $609,000), and *exported*:—

Crude petroleum	168,900,000 galls.	(value,	$5,277,000)
Light petroleum	77,650,000 ,,	(,,	6,302,000)
Illuminating oil	1,005,027,000 ,,	(,,	62,477,000)
Lubricating and heavy paraffin oil	170,430,000 ,,	(,,	20,891,000)
Residuum, tar, pitch, etc.	124,055,000 ,,	(,,	4,141,000)

The world's production of crude petroleum is shown by the following figures :—

	1894.	1908.
	Tons.	Tons.
United States	6,500,000	23,900,000
Russia	5,000,000	8,300,000
Galicia	130,000	1,750,000
Roumania	70,000	1,150,000
Dutch Possessions in the Indian Seas	115,000	1,140,000
Straits Settlements, etc.	44,000	670,000
Mexico	...	460,000
Japan	21,000	280,000
Germany	17,000	140,000
Peru	...	130,000
Canada	116,000	70,000
Total	12,000,000	38,000,000

The shale oil industry of Scotland is still important. In 1909 3,000,000 tons of oil shale were distilled, yielding 280,000 tons of crude oil, and 57,000 tons of ammonium sulphate. The crude oil on redistillation yielded 85,000 tons illuminating oil, 16,000 tons motor spirit, 40,000 gas oil, 40,000 tons lubricating oil, and 25,000 tons paraffin. The principal firm is J. Young, of Glasgow.

II.—MINERAL WAXES, INCLUDING ASPHALT AND BITUMEN

By G. Martin, Ph.D., M.Sc.

LITERATURE

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Paraffin wax is obtained from two principal sources—

1. From petroleum.
2. From bituminous shales.

Paraffin from Petroleum

The crude oil is distilled and its more volatile constituents removed, forming benzine and burning oil distillates. The residue is subjected to a further distillation in a special vacuum still. This consists of a cast-iron boiler A (Fig. 5), provided with an opening for charging, a safety-valve C, and an outlet tube D.

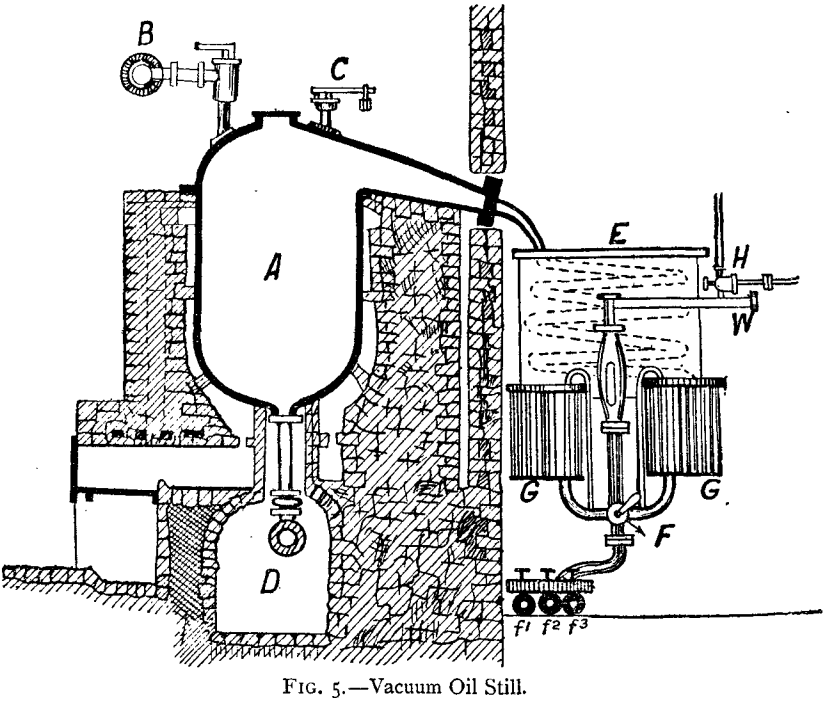

Fig. 5.—Vacuum Oil Still.

The distillate passes over into the coil E, which is immersed in a cold wat tank. Here it is condensed and flows through P into the reservoirs G and by way of the four-way tap F. A glass window commands a view of the di tillate as it flows from the coil. The apparatus is kept exhausted by a pow ful air-pump attached to H. The oil can be run away through the tubes f_1, f_2, The retort is heated by direct firing. When all the oil has distilled over, a mass fluid pitch remains behind in the retort, and is run away through D into small sti and is there subjected to considerably higher temperatures, being finally convert into coke.

The bulk of the thick, heavy, oily distillate from the "Residuum," very rich paraffin, is run while hot into closed "mixers," 3-5 per cent. of concentra sulphuric acid is added, and the fluid is churned up and thoroughly mixed by powerful air blast driven through it. A vigorous action takes place whereby th bases, sulphur compounds, and unsaturated hydrocarbons are either dissolved ou by the acid or converted into resinous matter, much sulphur dioxide is evolved.

The sulphuric acid "tar" at the bottom is run off, the oil freed from excess acid by washing with caustic soda solution and water, and the slimy mass is run i long, narrow, iron cylinders, and cooled to 15° C. by water. A mass of d coloured paraffin wax crystallises out, and is separated from the excess of oil forcing the whole under very high pressure through a filter press, which retains paraffin on the canvas sheets stretched through it, but allows the oil to flow aw The paraffin cakes thus obtained are compressed under 100-200 atmospheres hydraulic presses, and a further quantity of oil squeezed out. This crude sca still containing, say, 2·5 per cent. of oil, was formerly refined by repeatedly mixi with benzene, crystallising, and pressing the cake hydraulically. But this and oth processes have been superseded by the simple and cheap "sweating process discovered by Mr J. Hodges of Price's Patent Candle Co. (English Patent, No. 3, 1871). In modern practice this consists of allowing the crude scale to crysta slowly on a thin layer of water in shallow iron pans which are placed in tiers brickwork "oven" provided with steam coils. When sufficiently solid the w is run off and heat gradually applied. The oil and softer paraffins drain a leaving the harder paraffin much improved in colour. If desired, it may be a sweated to produce a harder paraffin, while the softer paraffins are recovered f the oily drainings by subjecting them to the same process. In all cases the so what yellow sweated cake remaining in the tray is melted out and agitated w successive quantities of some decolourising agent. This may be the "anim charcoal" recovered from the "melt" in prussiate of potash making, or Fuller earth, or similar powders, from which the refined paraffin is clarified by pumping through filter presses.

The crude scale obtained from filtering the oil at 15° C. may yield paraffin wax ranging from 65° to, say, 52° M.P. The oil from which this harder paraffin has been separated is cooled to −5° C., and a further deposit of softer scale separates. This, after purifying as above described, melts at 30°-45° C., and forms paraffin of the second quality.

It may be noted that the higher the melting point of the paraffin the greater its commercial value. Consequently the temperatures of working are so regulated as to obtain as great a yield as possible of high-melting paraffin.

Paraffin from Oil Shales and Bituminous Coal.

The Scottish oil shales yield, when distilled, large quantities of an oil very rich in paraffin. A considerable quantity of paraffin wax is also obtained from brown-coal tar, which is extensively worked in Germany. The general method o separation and purification is similar to that outlined above.

Paraffin is a mixture of solid hydrocarbons of the Paraffin Series. It forms a hard white translucent mass extremely inert chemically. Exposed to a slight pressure at a temperature below its melting point it becomes transparent, but

reverts to its usual translucent state on cooling or on being struck. The substance is odourless, tasteless, insoluble in water, slightly soluble in alcohol, easily soluble in ether, benzine, and carbon disulphide. According to its source its specific gravity varies from 0.86-0.91 at 15° C. and 0.74-0.76 at 100° C. When pure it can be distilled almost without decomposition. The best varieties melt between 56° C. and 65° C. Inferior varieties melt so low as 30° C., being at the same time soft, though still retaining their crystalline structure. Hard paraffin is used chiefly for making candles. It burns without smell and yields more light than the oxygen-rich stearin and beeswax. It has the defect of softening at a temperature below its melting point, and consequently must be hardened by mixing with stearic acid (5 per cent. and more). The softer sorts of paraffin are used for making wax matches, tapers, etc. etc.

Ozokerite, Ceresine, Earthwax.—Ozokerite or earthwax is the solid residue left behind when petroleum evaporates. It occurs in very large quantities, mixed with earth, in most oil-bearing districts. The most productive sources are in Galicia, where over 8,000 tons are mined yearly. Large quantities are found in the Caucasus and in North America. Immense unworked deposits exist on the island of Cheleken in the Caspian Sea.

The raw wax, mixed with earthy impurities, is melted in large iron boilers by means of hot water. The wax is drained away from the earthy residue and is known as "melted wax." The earthy residue left behind in the boiler is extracted with benzine and the wax thus obtained is called "extracted wax."

The crude wax thus prepared (melting between 60°-70° C.) is now heated to 140°-150° C. with 20-25 per cent. of fuming sulphuric acid in cast-iron boilers provided with mechanical stirrers. A vigorous action sets in and the wax separates into two layers, one practically pure ceresine and the other a black resinous mass containing most of the impurities. The heating is continued until all the sulphuric acid has been expelled as sulphur dioxide and the resinous layer completely decomposed into a charred mass. Next animal charcoal, bone black, fuller's earth, or other decolourising agent is stirred in, the melted wax filtered through hot steam-jacketed filter presses, and obtained as a yellowish mass. It is rendered perfectly white by repeating the treatment with sulphuric acid (using, however, less than before) and animal charcoal. The wax remaining in the decolourising powder is extracted with benzine.

The substance thus prepared is known as "*Ceresine.*" It resembles beeswax in appearance, being much less crystalline than paraffin. It melts between 60° and 70° C., and is sometimes used in conjunction with paraffin wax in candles. It can seldom be recommended, as most grades gutter and smoke freely. Sp. gr. 0.91-0.92 (15.5° C.).

Besides candlemaking, ceresine is used for preparing insulating compounds in electrical work, for making furniture and shoe polishes, for adulterating beeswax, and for making artificial vaseline (by mixing with oil). Its chemical constitution differs from that of paraffin, since it, apparently, consists of a mixture of olefines having the formula C_nH_{2n}.

Adulteration of Ceresine.—Owing to its high price ceresine is often adulterated with paraffin wax, bleached resin, and (in order to raise its melting point) small quantities of carnaüba wax.

(1) **Rosin** may be detected by boiling the wax with alcohol and titrating the alcoholic solution with standard KOH. 56.1 parts of KOH neutralise 346 parts of rosinic acids. Ceresine is a neutral body, but feebly soluble in alcohol, while rosin contains much acid matter, easily soluble in alcohol.

(2) **Paraffin** in ceresine may be detected by boiling with absolute alcohol, cooling, filtering a few drops of the alcohol on to an object glass, and examining under the microscope. If a crystalline residue separates paraffin is present, since ceresine is not crystalline, and is only very feebly soluble in alcohol.

To detect small quantities of ceresine in paraffin (put in to raise its melting point) dissolve 1 g. of sample in 10 c.c. carbon disulphide at 20° C. A clear solution shows that less than 10 per cent. ceresine is present. Now run 1 c.c. of the solution into a test tube containing 5 c.c. ether and 5 c.c. absolute alcohol (96 per cent.). Shake. Ceresine is present if white flocks separate. This test breaks down if the paraffin wax melts above 54° C. (Graefe, *Chem. Zeit.*, 1903, 248).

(3) **Carnaüba** wax is detected by saponifying with alcoholic caustic soda, and boiling the unsaponifiable residue with twice its weight of acetic anhydride under reflux condenser. Separate lower layer of acetic anhydride (which contains the waxy alcohols from the carnaüba wax) from the hydrocarbons floating on the surface, running the lower layer from a separating funnel into boiling water. Wash precipitate of the alcoholic acetates from the wax, dry at 100° C. and weigh.

Determine the saponification value (p. 62) of the mixed acetates, and isolate the alcohols by acidifying, filtering off the precipitated alcohols, and crystallising them from alcohol. Then take their melting points.

The mixed alcohols from carnaüba wax melt at 85° C. and their acetates have a saponification value of 123.

Asphalt or **Mineral Pitch** is probably the residue from the evaporation of petroleum as it exudes from the earth, changed by long contact with the atmosphere.

Trinidad and Bermudas asphalt have the approximate composition: C = 82.3 82.8 per cent.; H = 10.7 per cent.; S = 6 per cent.; N = 0.75-0.81 per cent.

In some parts of the Caucasus are hills of asphalt over 100 ft. in height, through which the black heavy oil still slowly exudes. Part of the island of Cheleken in the Caspian Sea is simply a vast mass of asphalt, the accumulated residue of thousands of tons of petroleum which have escaped in past times from the ground and evaporated *in situ*. But the most wonderful deposits in the world occur in Trinidad, where a regular lake of pitch, 127 acres in extent and of unknown depth, exists, and is mined for asphalt. Over 1,500,000 tons of pitch have already been removed from this lake, and 100,000 to 150,000 tons are yearly exported from Trinidad. Extensive deposits of a somewhat harder variety are also worked in the neighbourhood of the lake (La Brea).

Large deposits of asphalt occur in Cuba, Venezuela, Bermudas, California, Utah, Texas, Canada, and parts of Europe.

Asphalt is much used for paving streets, making black varnishes, for electrical insulators, as a protective paint for the interior of chlorine stills and acid tanks, and for waterproofing. A product very similar to natural asphalt may be produced by blowing air through the hot residues left in petroleum stills.

Montan Wax is a white substance prepared from bitumen extracted from lignite by means of volatile solvents. It melts at 80°-86° C. and is used as a carnaüba wax substitute in the manufacture of polishes, and as an insulating material in place of ceresine. When distilled with superheated steam it yields white "**Montanic Acid**," M.P. 70°-80°—a mixture of fatty acids and hydrocarbons. The still residues—montan pitch—are used as insulators and for gramophone cylinders. The proposal to use montan wax as candle material and even as candle stiffeners has not been very successful. (See English Patent, 5,999, 1900; German Patents, 101,373, 116,453, 202,909; *Zeit. für Angewandt. Chem.*, 1901, No. 44, p. 1110.)

Statistics.—In 1910 England *exported* 290,000 cwt. of paraffin wax (*value*, £288,000) and *imported* 1,064,000 cwt. (*value*, £1,017,000). In the same year 69,000 *tons* of asphalt or bitumen (*value* £169,700) were imported. The Scottish shale oils yielded in 1909 about 500,000 cwt. of paraffin wax.

The figures for the United States for 1910 were:—

	Imports 1910.
Paraffin and Paraffin Wax - - -	7,082,000 lbs. (value $334,000).
Asphaltum and Bitumen - - -	146,000 tons (value $712,000).

	Exports 1910.
Paraffin and Paraffin Wax - - -	196,980,000 lbs. (value $7,886,000).
Asphaltum and Bitumen - - -	19,600 tons (value $488,000).

The author's best thanks are due to Messrs Price & Co. for kindly reading through the article, also to Mr W. H. Stephens, A.R.C.S., for expert advice and assistance.

For **Vegetable Waxes** see p. 60.

III.—THE MANUFACTURE, AND PROPERTIES AND USES OF ANIMAL AND VEGETABLE OILS, FATS, AND WAXES, INCLUDING LINSEED OIL; AND THE MANUFACTURE OF VARNISHES, ENAMELS, OILCLOTH, AND LINOLEUM

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INTRODUCTION

Fats and fatty oils occur disseminated throughout the tissues of almost all animals and seeds in the form of minute globules enclosed within a thin skin, forming a reserve food for the organism. Pressure alone will not usually suffice to break up the animal fat cells; the tissue must be heated when it shrivels up as it loses water, while the increasing temperature causes the fat globules to expand, burst the cell, and flow out as a liquid mass. In the case of vegetable seeds pressure alone often secures the expulsion of the oil although here, too the operation is much facilitated by a gentle heat.

The difference between a fatty oil and a fat is merely one of physical condition due to temperature; an oil freezes into a fat, and a fat melts to an oil. In a warm climate a substance will always appear as an "oil," whereas the same body will appear to the inhabitants of a colder clime as a solid fat. Thus, for example, cocoanut oil is liquid in India but solid in England, where it is used by vegetarians in place of butter. As previously explained, "mineral" oils are quite different in chemical character to a vegetable or animal oil.

Chemically considered, fats and fatty oils are bodies produced by the chemical union of glycerol with fatty acids. *Glycerol* is a trihydric alcohol, of formula $C_3H_5(OH)_3$. It is capable of combining with three molecules of fatty acids to form "triglycerides," thus :—

$$\begin{matrix} .OH \\ C_3H_5.OH \\ .OH \end{matrix} + 3.R.OH = \begin{matrix} .OR \\ C_3H_5.OR \\ .OR \end{matrix} + 3H_2O$$

Glycerol. Fatty Acid. Triglyceride of Fatty Acid. Water.

Where R stands for the radicle of the fatty acid.

Fats and fatty oils are merely mixtures of these triglycerides of the fatty acids. The three glycerides which usually predominate in most fats are solid tristearin, solid tripalmitin, and liquid triolein—the respective glycerides of stearic, palmitic, and oleic acids. Solid fats usually contain much stearin and palmitin, but little olein; liquid fats, on the other hand, consist principally of olein. Other fats and oils exist (*e.g.*, linseed and castor oils) which are composed of glycerides of other acids than those mentioned above. We append a list of the principal fatty acids occurring in natural fats and oils, together with the names and formulæ of their triglycerides.

Fatty Acids and their Triglycerides

Saturated Acids of the Acetic Series. $C_nH_{2n+1}.COOH$.

Acid.	Formula.	M.P. (° C.)	B.P. (° C.)	Corresponding Glyceride.	Formula.
Formic	$H.COOH$	8.3	101	Formin	$C_3H_5(O.HCO)_3$
Acetic	$CH_3.COOH$	16.5	118	Acetin	$C_3H_5(O.CH_3CO)_3$
Propionic	$C_2H_5.COOH$	−22.0	141	Propionin	$C_3H_5(O.C_2H_5CO)_3$
Butyric (normal iso)	$C_3H_7.COOH$	−7.9	162	Butyrin	$C_3H_5(O.C_3H_7CO)_3$
		−79.0	154		
Valeric (normal iso)	$C_4H_9.COOH$	−58.5	185	Valerin	$C_3H_5(O.C_4H_9CO)_3$
		−51.0	174		
Caproic	$C_5H_{11}.COOH$	−8.0	205	Caproin	$C_3H_5(O.C_5H_{11}CO)_3$
Aethanthylic	$C_6H_{13}.COOH$	−10.0	223	Aethanthylin	$C_3H_5(O.C_6H_{13}CO)_3$
Caprylic	$C_7H_{15}.COOH$	16.5	237.5	Caprylin	$C_3H_5(O.C_7H_{15}CO)_3$
Perlargonic	$C_8H_{17}.COOH$	12.5	186	Perlargonin	$C_3H_5(O.C_8H_{17}CO)_3$
Capric	$C_9H_{19}.COOH$	31.3	200	Caprin	$C_3H_5(O.C_9H_{19}CO)_3$
Undecylic	$C_{10}H_{21}.COOH$	28.0	212	Undecylin	$C_3H_5(O.C_{10}H_{21}CO)_3$
Lauric	$C_{11}H_{23}.COOH$	43.6	225	Laurin	$C_3H_5(O.C_{11}H_{23}CO)_3$
Tridecylic	$C_{12}H_{25}.COOH$	40.5	236	Tridecylin	$C_3H_5(O.C_{12}H_{25}CO)_3$
Myristic	$C_{13}H_{27}.COOH$	53.8	248	Myristin	$C_3H_5(O.C_{13}H_{27}CO)_3$
Pentadecatoic	$C_{14}H_{29}.COOH$	51.0	257	Pentadecatoin	$C_3H_5(O.C_{14}H_{29}CO)_3$
Palmitic	$C_{15}H_{31}.COOH$	62.0	268	Palmitin	$C_3H_5(O.C_{15}H_{31}CO)_3$
Margaric	$C_{16}H_{33}.COOH$	60.0	277	Daturin	$C_3H_5(O.C_{16}H_{33}CO)_3$
Stearic	$C_{17}H_{35}.COOH$	69.3	287	Stearin	$C_3H_5(O.C_{17}H_{35}CO)_3$
Nondecylic	$C_{18}H_{37}.COOH$	66.5	298	Nondecylin	$C_3H_5(O.C_{18}H_{37}CO)_3$
Arachidic	$C_{19}H_{39}.COOH$	77.0	...	Arachidin	$C_3H_5(O.C_{19}H_{39}CO)_3$
Medullic	$C_{20}H_{41}.COOH$	...	...	Medullin	$C_3H_5(O.C_{20}H_{47}CO)_3$
Behenic	$C_{21}H_{43}.COOH$	83.0	306 (60 mm.)	Behenin	$C_3H_5(O.C_{21}H_{43}CO)_3$
Carnaübic	$C_{23}H_{47}.COOH$	72.5	...	...	... ...
Hyaenic	$C_{24}H_{49}.COOH$	77.5	...	...	... ...
Cerotic	$C_{26}H_{53}.COOH$	78.0	...	...	... ...
Melissic	$C_{29}H_{59}.COOH$	91.0	...	...	... ...

(At 100 mm. pressure.)

FATTY ACIDS AND THEIR TRIGLYCERIDES—*continued*

Unsaturated Fatty Acids of the Oleic Series. $C_nH_{2n-1}COOH$.

Acid.	Formula.	M.P. (° C.)	B.P. (° C.)	Corresponding Glyceride.	Formula.
Acrylic	$C_2H_3.COOH$	+13	140	...	...
Crotonic	$C_3H_5.COOH$	71.5	180.5	...	...
Iso-crotonic	$C_3H_5.COOH$	15.5	169	...	...
Angelic	$C_4H_7.COOH$	45	185	...	...
Tiglic	$C_4H_7.COOH$	65	198	...	...
Hypogaeic	$C_{15}H_{29}.COOH$	...	...	...	$C_3H_5(O.C_{15}H_{29}CO)_3$
Oleic	$C_{17}H_{33}.COOH$	14	223 (10 mm.) or 250 (superheated steam)	Olein	$C_3H_5(O.C_{17}H_{33}CO)_3$

Unsaturated Fatty Acids of the Linolic Series. $C_nH_{2n-3}COOH$.

Elaeostearic (Elaeomargaric)	$C_{16}H_{29}.COOH$	43	...	Elaeostearin	$C_3H_5(O.C_{16}H_{29}CO)_3$
Linolic	$C_{17}H_{31}.COOH$	below −18	...	Linolein	$C_3H_5(O.C_{17}H_{31}.CO)_3$

Unsaturated Fatty Acids of the Linolenic Series. $C_nH_{2n-5}COOH$.

Linolenic	$C_{17}H_{29}.COOH$	Liquid	...	Linolenein	$C_3H_5(O.C_{17}H_{29}.CO)_3$

Unsaturated Fatty Acids of the Recinoleic Series.

Recinoleic	$C_{17}H_{32}(OH).COOH$	4	...	Recinolein	$C_3H_5(O.C_{17}H_{32}(OH).CO)_3$

It may be noticed that monoglycerides and diglycerides, corresponding to the formulæ $C_3H_5\begin{matrix}.OR\\.OH\\.OH\end{matrix}$ and $C_3H_5\begin{matrix}.OR\\.OR\\.OH\end{matrix}$, exist in rancid or partially hydrolysed fats, while mixed glycerides of the formula $C_3H_5\begin{matrix}.OR_1\\.OR_2\\.OR_3\end{matrix}$ (R_1, R_2, R_3, corresponding to three different acid radicles) certainly occur in small quantities in certain normal fats, *e.g.*, in ordinary butter-fat, also in tallow.

Fats are usually neutral bodies, but old or rancid fats often contain large quantities of free fatty acids, which may be extracted by sodium carbonate solution or by alcohol. Old palm oil, and some fish oils, often contain no less than 60 per cent. of free fatty acids.

While at ordinary temperatures some fats are white crystalline solids, others are fluids, fatty to the touch; all produce permanent grease-spots on paper; they are insoluble in water, slightly soluble in alcohol, easily soluble in ether, benzine, chloroform, carbon disulphide, and carbon tetrachloride. When distilled alone they decompose, producing vapours of acrolein; with high tension steam they distil with partial saponification into free acids and glycerol.

Pure fats are tasteless, odourless, and keep for years. When, however, they contain small quantities of nitrogenous animal or vegetable impurities they often turn rancid in the presence of air, decomposing into free acids and glycerol by a process of enzyme hydrolysis. Oxygen is absorbed during this change, and the acids formed are often oxidised to oxyacids, while the glycerol is also partially destroyed. In air-tight vessels, in the absence of oxygen, fats do not become rancid.

When heated with an aqueous (but best with an alcoholic) solution of sodium or potassium hydroxide fats are completely "saponified" into glycerol and the alkali salt of the fatty acid, thus:—

$$\underset{\text{Tristearin.}}{C_3H_5(O.C_{17}H_{35}CO)_3} + \underset{\text{Caustic Soda.}}{3NaOH} = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Sodium Stearate (ordinary soap).}}{3C_{17}H_{35}.COONa}$$

The metallic or inorganic salts of the fatty acids are called "soaps."

Other bases, such as slaked lime, magnesia, and lead oxides, readily saponify most fats, the resultant soaps, however, being usually insoluble.

It should be particularly noticed that the alkali carbonates, such as sodium or potassium carbonates, will not saponify fats even when boiled with them at ordinary pressures. Heated under high pressure in autoclaves they readily saponify (see p. 108).

STATISTICS RELATING TO MINERAL, ANIMAL, AND VEGETABLE OILS AND FATS IMPORTED INTO THE UNITED KINGDOM. (For details regarding Mineral Oils, see pp. 13, 14.)

ARTICLES.		Quantities.		Value in 1910.
		1906.	1910.	
				£
Oil, Fish: viz., train, blubber, sperm, or head matter	Tuns	27,808	46,101	927,231
,, Animal	Cwt.	165,659	105,571	146,654
,, Castor	,,	50,329	26,898	39,334
,, Cocoa-nut: unrefined	,,	335,545	539,686	1,013,629
,, ,, refined	,,	202,491	500,219	1,136,736
,, Mineral jelly (including vaseline)	,,	...	21,773	47,960
,, Olive: unrefined	Tuns	9,419	6,905	299,922
,, ,, refined	,,	4,967	6,311	386,189
,, Palm: unrefined	Cwt.	1,223,787	1,994,385	3,056,614
,, ,, refined	,,	61,684	60,775	111,800
,, Mineral and lubricating (for details see p. 13)		...	...	5,653,802
,, Seed—				
Cotton-seed oil: unrefined	Tons	1,786	902	22,984
,, ,, refined	,,	10,884	15,950	562,672
Linseed oil: pure	,,	17,056	37,242	1,252,141
,, not pure	,,	1,508	1,221	25,477
Rape-seed oil	,,	11,050	13,489	359,166
Other seed oils	,,	4,627	12,455	398,597
,, Turpentine	Cwt.	512,836	472,247	1,001,216
,, Essential: natural	Lbs.	1,882,080	1,983,063	320,218
,, ,, artificial	,,		169,599	34,369
,, Unenumerated	Value	...	...	160,741
Total of oil		...	...	16,966,532
Oleo-margarine or oleo oil	Cwt.	291,932	448,215	1,116,383
Tallow and stearin	,,	1,933,836	2,462,771	4,194,489
Lard	,,	2,049,367	1,452,493	4,520,074
Oil-seed cake, containing no dutiable ingredient—				
Cotton-seed cake	Tons	155,160	157,277	952,884
Linseed cake	,,	167,791	104,210	860,015
Rape-seed cake	,,	13,229	23,169	111,034
Other sorts	,,	24,018	32,410	185,671
Total of oil-seed cake		360,198	317,066	2,109,604
Nuts and kernels, for expressing oil therefrom	Tons	57,265	95,950	1,915,279

Superheated steam or hot acids "hydrolise" fats into glycerol and free fatty acids, thus :—

$$\underset{\text{Tristearin.}}{C_3H_5(OC_{17}H_{35}CO)_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Stearic Acid.}}{3C_{17}H_{35}.COOH}$$

Certain ferments present in seeds (especially in castor seeds) readily split fats into glycerol and fatty acids at ordinary temperatures. See under *Candles*, p. 93.

The fats and fatty oils are used for making soap, candles, lubricants, varnishes, paints, for burning in lamps, and for edible purposes. The industry is an enormous one.

Fats have been artificially synthesised; for recent work see Grün and collaborators, *Ber.*, 1907, xl., 1778-1791, 1792-1801, and later papers.

The following numbers refer to the *Exports* from the United Kingdom :—

Articles.	Quantities.		Value in 1910.
	1906.	1910.	
			£
Oil, other than essential, or medicinal—			
,, Cocoa-nut: unrefined - - - Cwt.	30,236	73,173	126,710
,, ,, refined - - - - ,,	13,730	228,109	430,663
,, Olive: unrefined - - - - Tuns	23	22	1,354
,, ,, refined - - - - ,,	112	368	49,125
,, Palm: unrefined - - - - Cwt.	2,583	48,214	84,801
,, ,, refined - - - - ,,	17,162	13,710	23,458
,, Seed—			
Cotton-seed oil: unrefined - - Tons	159	411	11,979
,, ,, refined - - ,,	26,155	29,501	874,571
Linseed oil: pure - - - ,,	21,954	21,463	837,712
,, not pure - - - ,,	2,403	3,021	98,851
Rape-seed oil - - - - ,,	3,928	5,052	141,368
Other seed oils - - - - ,,	459	38,944	1,122,146
Other sorts, unenumerated - - Value	...	...	1,561,634
Total of oil - - - ,,	...	...	5,364,372
Oil-seed cake, not sweetened—			
Cotton-seed cake - - - - Tons	21,432	10,150	49,613
Linseed cake - - - - ,,	450	682	5,021
Rape-seed cake - - - - ,,	1,822	...	...
Other sorts - - - - - ,,	2,423	164,590	1,032,549
Total of oil-seed cake, not sweetened - - ,,	26,127	175,422	1,087,183
Oleo-margarine - - - - - Cwt.	10,705	81,381	206,360
Grease, tallow, and animal fat - - - ,,	726,697	719,705	...

The following statistics show the magnitude of the industry in the **United States**:—

IMPORTS IN 1910.

Article.	Quantity.	Value.
Fish oils - - - - - - - -	2,311,000 gals.	$727,000
Cocoa butter, butterine - - - - -	3,369,000 lbs.	679,000
Cocoanut oil - - - - - - -	48,345,000 ,,	3,341,000
Hemp- and rape-seed oil - - - - -	1,082,000 ,,	464,000
Nut ,, ,, - - - - - -	5,759,000 gals.	2,440,000
Olive oil (free) - - - - - -	842,000 ,,	477,000
,, (dutiable) - - - - - - -	3,702,000 ,,	4,869,000
Palm oil - - - - - - - -	92,771,000 lbs.	5,590,000
Oleo steam - - - - - - - -	7,684,000 ,,	901,000

EXPORTS IN 1910.

Article.	Quantity.	Value.
Fish oils	1,529,000 gals.	$370,000
Lard oils	151,000 ,,	131,000
Other rendered oils	535,000 ,,	401,000
Corn oil	11,299,000 lbs.	643,000
Cotton-seed oil	223,955,000 ,,	14,798,000
Linseed oil	228,426 gals.	155,000
Oil-seed cake—		
Corn-seed cake	49,108,000 lbs.	689,600
Cotton-seed cake	640,088,000 ,,	9,071,000
Linseed or flax-seed cake	652,316,000 ,,	9,489,000
Beef tallow	29,380,000 ,,	1,780,000
Lard	362,928,000 ,,	43,301,000
Lard substitutes	74,556,000 ,,	6,888,000
Oleo oil	126,091,000 ,,	14,305,000
Oleo margarine	3,419,000 ,,	350,000

Manufacture of Animal Oils and Fats

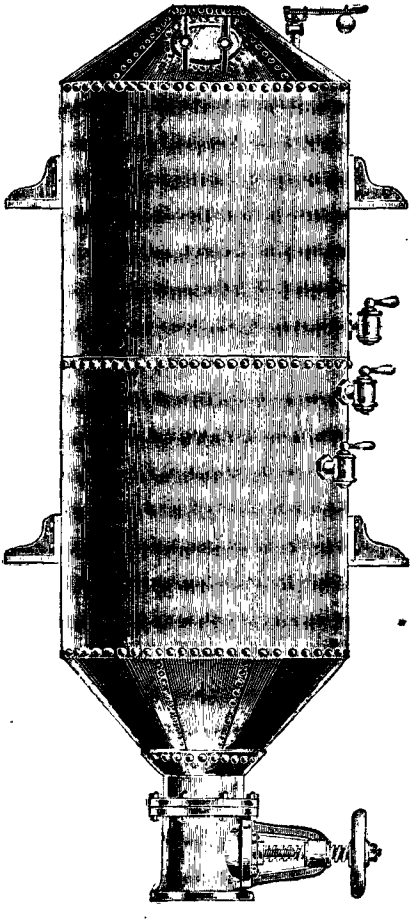

FIG. 6.—Packer's Rendering Tank.

These are usually obtained by heating the tissues rich in oil or fat, so as to cause the bursting of the fat-containing cell.

Tallow (beef or mutton fat).—The "rough fat" fresh from the slaughter-house is placed in a lead-lined tank provided with a steam coil for heating, and an outlet passing to a chimney stack for the escape of offensive vapours. Hot water is poured on to the fat, and the vessel and its contents heated for some hours by the steam coil. On settling, the melted fat rises to the surface as a clear layer, and is drawn off through outlet taps into another vessel. The fat is now ready for use, unless when made from inferior materials, when it must be refined and bleached as described below.

The residue of fatty matter left in the tank is acidified with a little sulphuric acid, and steam again turned on. The small amount of sulphuric acid does not hydrolyse the fats, but partially destroys the cell membranes, thus setting free their occluded fat, which is run off as before into another vessel. An inferior variety of fat is thus obtained.

Tallow for **soap making** (but not for comestible purposes) is rendered in digesters under pressure. Fig. 6 shows one of the large modern rendering tanks used in the American packing industry; made of riveted steel plates and capable of standing a working pressure of four or five atmospheres, the largest ones are 8 ft. in diameter and 20 ft. high. They are provided with safety-valves, and discharge through a gate valve at the bottom. The tank is filled to within a foot of the junction

of the upper cone and the cylindrical portion of the vessel — the material (in Chicago) often consisting of putrid carcasses of animals which have died in transit, diseased flesh, and other waste products unfit for comestible products. Then live steam at 40-50 lbs. pressure is turned on, and the contents of the boiler heated for eight to ten hours or so, the internal temperature being maintained at 130°-140° C. Two air-cocks carry away the offensive fumes evolved during the heating. Finally the steam is turned off, the vent-pipes opened to allow the steam in the tanks to blow off, and the fat is allowed to settle. The clear liquid fat floating on the surface of the water in the tank is now drawn off through the top draw-off cock, and, as the level in the tank subsides, through the lower ones in succession. Finally, water is pumped in from below, so as to raise the level of the fat (which, of course, floats upon the water) so that it too may be withdrawn through the stopcocks.

Last of all the valve at the bottom of the tank is opened, and the contents run out into a series of settling tanks and catch basins to retain fat globules still in the water. A sludge settles at the bottom of these tanks; it is drawn off and pressed. The liquid running from the tanks flows into evaporators (vacuum, triple effect)

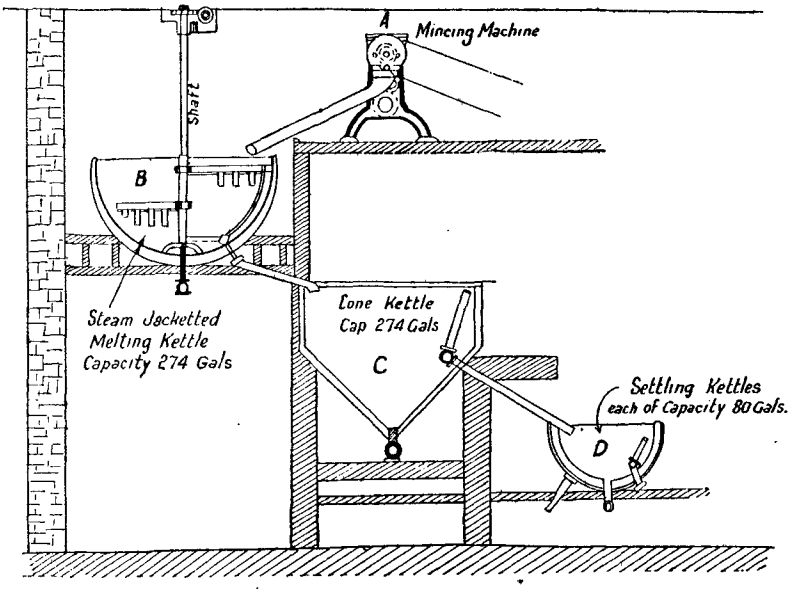

FIG. 7.—Manufacture of Oleo Stearin and Oleo Oil from Beef Fat.

here it is boiled down into a thick "soup." The sludge press-cakes are now mixed ith this, and the mass sold as "Tankage Fertiliser."

Lard is the fat of the hog, which is separated from the slaughtered animal, nd worked up as described above.

Manufacture of Oleo Stearin and Oleo Oil from Beef Fat

The fat from the recently slaughtered animal is rapidly removed and plunged nto a vat, and washed with warm water until free from blood and other impurities, ardened by immersion in ice water, chopped into a fine mass by a machine A (Fig. 7), nd melted at 70°-75° C. in a steam-jacketed pan B, provided with slowly moving echanical agitators. The mass is allowed to settle, salt being strewn over the urface of the liquid in order to accelerate the settling out of membranes and con-ective tissue (which collect at the bottom). Next the clear oil is siphoned over to nother series of melting kettles, C, usually situated on a lower floor. More salt

is added, and the temperature maintained at 70°-80° C. until a second settling is complete. The fat, now free from membrane and connective tissue, is siphoned into shallow settling tanks and allowed to stand three to five days at a temperature (peculiar to each fat) which experience shows is best suited for allowing the stearin to crystallise. This stearin forms a crust over the surface, and the rest settles at the bottom, leaving a clear oil between. The crystallisation completed, the crust is broken into fine fragments by vigorous mechanical stirring, and the pasty mass thus obtained conveyed to a revolving table surrounded by skilled workmen, who wrap the mixture into small packages in canvas cloth (each containing about 3 lbs. weight), place them in hydraulic presses, and separate the oleo oil by great pressure slowly applied. The oil flows from the presses into large receiving tanks, while the solid stearin remains in the press as a cake, which is mixed with cotton-seed oil, and used for making lard substitute. The oleo oil is converted into margarine as described on p. 85. Caul fat yields about 50 per cent. oleo oil and 30 per cent. solid stearin, the precise yield varying considerably according to the temperature of pressing, the amount of tissue, and the quality of fat.

Lard Stearin and Lard Oil are obtained by treating hog fat (lard) as above described. The oil is used for illuminating purposes, and the stearin for the manufacture of lard compound and soap.

Fat from Garbage.—In large cities a considerable quantity of fat for soap-making is made by heating sewage or garbage in upright steel tanks of 6 ton capacity with live steam at 30 lbs. pressure for six to eight hours. The mass is ru into vats, allowed to settle, and the free water and grease floating on it are run by drop-pipes into separating tanks. The sludge is filtered through cloth, and t cakes of solid matter compressed and sold as manure.

Fish Oils are obtained from all parts of the body of common fish—such sardine, salmon, sprat, herring, menhaden, etc., by boiling. The best sorts of **Co Liver Oil** are prepared by heating the livers (taken from the fish brought asho alive and treated the same day) of the cod fish in steam-jacketed vessels, when t cell membranes burst and the oil exudes. Inferior qualities are obtained by trea ing the putrid livers in a similar way; although unfit for medicinal purposes it largely used in the leather industry (see Dégras). **Seal** and **whale oil** are extracte from the blubber of the animals, sometimes on board ship itself, but more often i "trying" stations situated in Finnmarken, on the Lofotes, and in Iceland. Th blubber is stripped clean from the flesh immediately after the arrival of the shi cut into strips, chopped in mincing machines, delivered into melting pans, a boiled with steam.

Menhaden Oil is prepared from the heads and intestines of fish, especia of the menhaden or mossbanker of the Atlantic coast of America; used in t leather, paint, and rope trades.

For **Sperm** and **Arctic Sperm Oil** see under **Liquid Waxes.**

Manufacture of Vegetable Oils

Vegetable oils and fats are obtained from oil-bearing substances (usually seed by two distinct processes: *—

(*a*) By pressing in hydraulic presses.
(*b*) By extracting with volatile solvents.

(*a*) Oil Extraction by Pressure

Four distinct operations are usually performed:—

(1) The seed is crushed or ground in special machines so as to break th oil cells.

* For blocks and illustrations of machinery employed in seed-crushing, the authors have pleasu in thanking Messrs Rose, Downs, & Thompson, of Hull.

(2) The ground seed is heated so as to facilitate the flow of oil and to coagulate the albumen.

(3) The product is now gently pressed in a moulding machine to prepare it for the hydraulic press.

(4) Finally, the seed is conveyed to hydraulic presses and the oil expressed.

Two different sorts of presses are used, viz., the Anglo-American (plate) and the cage or "cylinder" (clodding) presses. In the Anglo-American system (Fig. 8) the moulded seeds are wrapped in cloth bags and placed between a series of plates. The expressed oil runs down, and is collected in tanks below the press. In the "cage" system (Fig. 9) the seeds are confined in a closed chamber perforated with little holes, large enough to allow the oil to flow out, but small enough to retain the seed. The pressure being applied, the oil is forced out. The advantages of the latter system are:—

(1) Very great pressures can be applied, so that nearly all the oil is extracted at a single pressing.

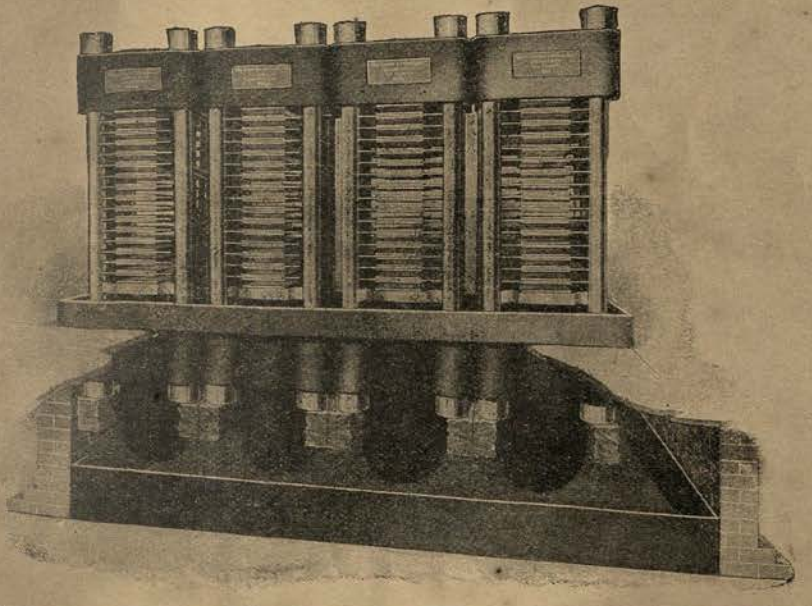

FIG. 8.—Battery of Four Anglo-American Oil Presses, having a continuous gutter for collecting the expressed oil. (Rose, Downs, & Thompson, of Hull.)

(2) No exudation of the mass from the edges of the cloths or bags occurs as in e Anglo-American system.

(3) The press cakes need not be "pared."

The plate or Anglo-American system is usually employed for the treatment of eds requiring one pressing. A combination of both systems is often employed r very oily seeds requiring two pressings, or for the production of two qualities oil.

Different seeds require a somewhat different treatment; linseed and cotton seed, r example, require one crushing, while castor seed and copra (the flesh of the coa-nut) are usually crushed twice. We will outline the process usually employed the case of the more important seeds.

Linseed.—The seed must be perfectly clean. It was formerly always necessary pass it through a screening machine to remove impurities; but now much of e linseed on the market is sold on the basis of 95 per cent. purity, and some at

97 per cent.; such seed is ready for immediate use without further cleaning. The clean seed is now passed to the rolls or crushing machinery C (Fig. 10, which represents a complete oil mill designed by Rose, Downs, & Thompson, of Hull). The seed is passed into the hopper in the usual manner, and is distributed to the crushing rolls (made of hardened chilled iron) by a fluted feed roller of the same length as the crushing rolls placed at the bottom of the hopper. The feed of the

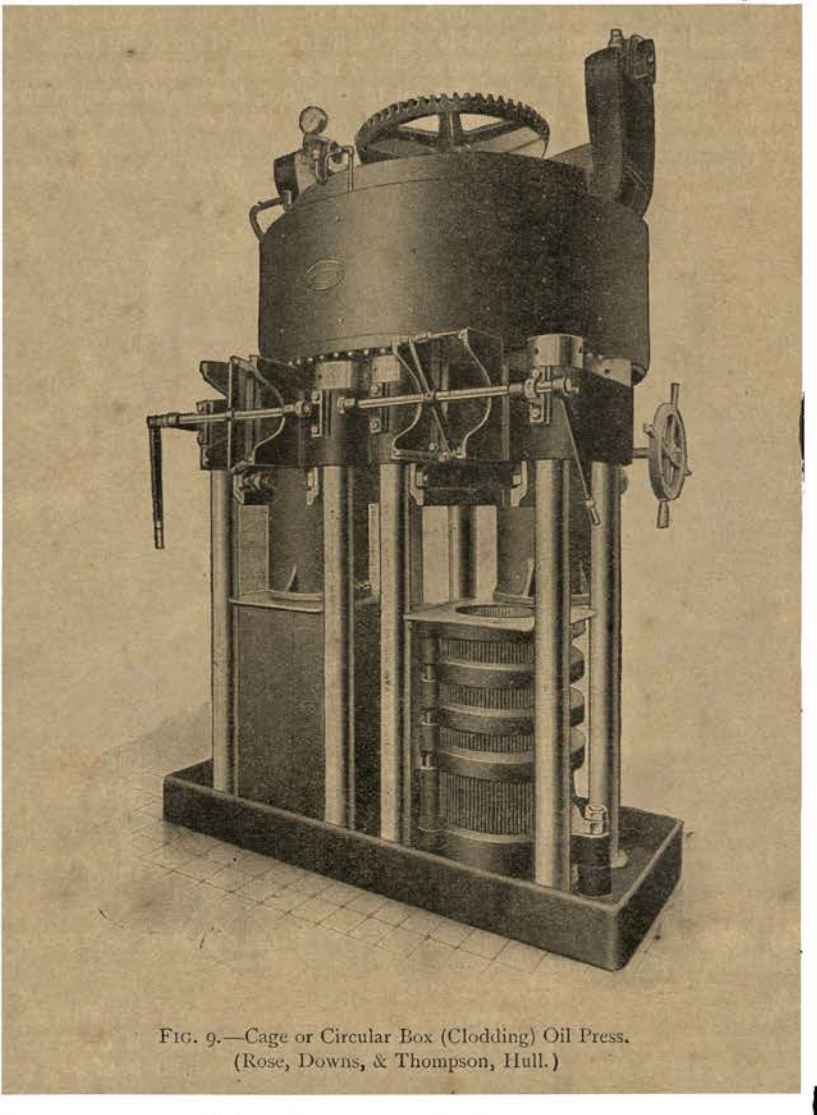

FIG. 9.—Cage or Circular Box (Clodding) Oil Press.
(Rose, Downs, & Thompson, Hull.)

seed to the rolls can be altered at pleasure. As the seed passes the feed roll, it fa
on to a guide-plate that carries it between the first and second rolls. After passi
between these and being partially crushed, the seed falls on to a guide-plate on t
other side, and is carried between the second and third rolls, where it is furth
crushed. It then falls on another guide-plate, which carries it between the thi
and fourth rolls, where it is ground still more. In large rolls it can be carri
between a fourth and fifth roll before it receives the final crushing.

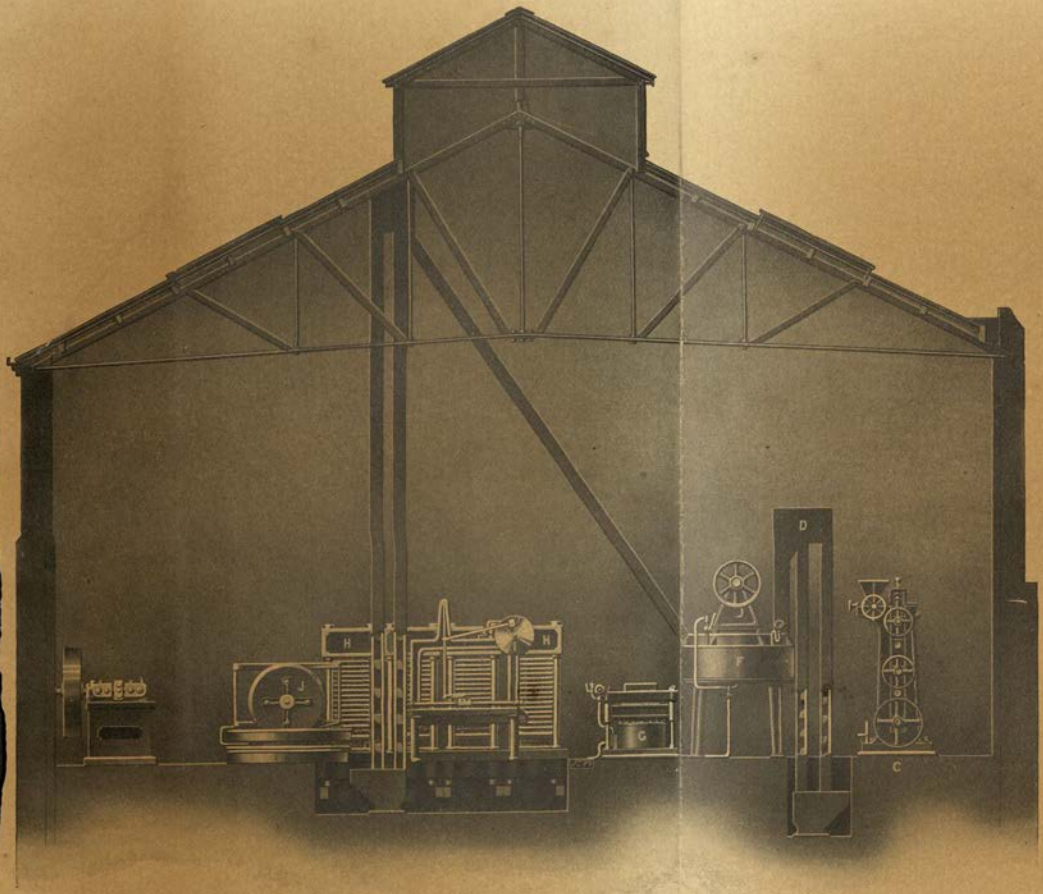

FIG. 10.—A COMPLETE ANGLO-AMERICAN OIL MILL. (Designed by Rose, Downs, & Thompson, of Hull, England.)

In the above illustration the complete process is shown. The seed passes through the rolls C; from these an elevator D places it in the kettle F, from which it passes into the moulding machine G, where it is measured, formed, and compressed; and thence it passes to the presses H. The cakes, after being pressed, are cut to size in the paring machine I, and the parings reduced to meal by the small edge-stones J. The parings are returned, to be reworked, to the kettle F.

The presses H stand in a tank into which the expressed oil falls, from whence it is forced to the stove-tanks, or filters, by a pump.

[*To face page* 28.

The crushed seed or meal is now raised by the elevator D (Fig. 10) into the kettle or heater F, where the mass is warmed by steam to the right temperature in order to facilitate the flow of oil when in the press, the heat also serving to coagulate albuminous matter in the grain. From the kettle the heated grain falls into the moulding machine or former G, where it is squeezed into cakes suitable for placing in the hydraulic press. The moulding machine also serves to accurately measure the amount of crushed or heated meal required for a cake, thus ensuring the production of cakes with little variation in weight.

The cakes thus formed are wrapped in cloth bags and placed in the hydraulic press (Fig. 8, and H, Fig. 10). One of the larger Anglo-American presses will take some sixteen cakes 28 in. by 12 in. each, separated from each other by a steel plate. When the press is full the pressure is slowly turned on, and the oil begins to flow from the compressed meal, at first slowly and then very rapidly, the oil running down the sides of the machine into a tank in which the presses stand, and from which it is forced by a pump to the filters or store tanks. When the pressure has been applied for three or four minutes the flow of oil practically ceases, the oil simply dripping from the compressed cakes until the pressure is released. If more presses than one are being used, they are filled one after the other until the whole battery of presses are charged. The meal cakes are allowed to remain under pressure from ten to forty minutes (the exact time varying with the special conditions) and then the pressure is released on the first press in the series and the ram allowed to descend. The cakes are removed one by one as the ram descends, and fresh charges of meal introduced wherever a cake is removed. The cakes as they are removed are placed on the paring machine, their cloth bags stripped off, and their oily edges cut away by the paring machine, these oily parings being reduced to meal again by small edge-stones J (Fig. 10), and returned to the kettle F (Fig. 10) to be worked up again. If a cage or circular box (clodding) press is employed the cake need not be pared—one great advantage of the latter system. The finished cakes are placed on racks in which they are allowed to stand until perfectly cool, when they are removed to the cake-house or store. The cake racks are usually placed in the most draughty part of the mill to assist the cooling process. Other similar small seeds are treated in much the same manner as linseed. Among these we may mention sunflower, mustard, China or Soya beans, some kinds of rape seed, poppy seed, and similar seeds requiring but a single pressing.

Cotton Seed also requires but a single pressing. Two varieties exist—the k seed and the white; the former has its husk quite clean and free from adherent on (example, Egyptian cotton seed), while the husk of the latter is covered with t white cotton fibres (examples, American cotton seed, Indian cotton seed). n classes of seed are treated in England in much the same way as linseed, the difference being that the seeds as they leave the rolls are ground beneath erful edge-stones before passing on to the kettles. In the United States, how- , the cotton seed is first decorticated, *i.e.*, the husk of the seed is entirely oved, only the resulting kernels or "meats" being pressed. The advantage this treatment becomes obvious when it is realised that practically 50 per cent. the seed is husk, and that consequently a mill removing this by using decorti- tors can treat twice as much seed as a mill of the same size, but without decorti- tors. The husks are used as cattle food, fuel, or manure, as the case may be.

Castor Seed.—This seed, being very rich in oil, is usually worked twice, the t time cold, and the second time hot. The seed must be very well cleaned fore pressing, which operation is best carried out in cage presses, the seed ing pressed in its natural state without any preliminary crushing at all. The st medical oil is the cold-drawn, and consequently it is greatly to the advantage oil manufacturers to press out as much oil as possible at a single pressing. mense presses have been erected for this purpose in some mills. A set of four nt presses is shown in the plate (Fig. 11), which represents a modern and improved e of press battery, designed by Rose, Downs, & Thompson, and used in some

large English oil mills. Each set comprises two presses, having cages or cake chambers 19 in. diameter and 9 ft. long internally. These chambers are finely perforated, so that while retaining the solid residue, they allow the oil and other fluids to escape. Each press has its own kettle, 60 in. by 26 in., while the rams are forced at a pressure of 3 tons on the square inch. The seed is fed whole to the kettles, are there heated by steam to about 32° C., and afterwards pressed at 3 tons on the square inch. The resulting cakes contain from 8.5 to 10 per cent. of oil. The whole battery of four presses is worked by two men, and press a total weight of 2 tons of seed per hour.

Presses of this type are specially suitable for the first pressing of all kinds of very oily seeds, such as castor, sesame, ground nuts, copra, palm kernels, etc., producing a maximum quantity of first pressing oil, and reducing the oil in the cakes to such small proportions as to render a second pressing unnecessary, or permitting the remaining available oil to be extracted by solvents. In view of the high prices commanded by first-pressure oil, such presses effect a very great economy, although the first cost is high. In mills where less powerful presses are employed, the solid cakes resulting from the first pressing are ground up in suitable machinery, warmed, and pressed again.

A very effective modern process is to first press with a cage machine, and then extract the bulk of the oil from the resulting cake by solvents. Such extracted oil cannot be used for edible purposes, but is valuable for soap-making, lubricating, etc. The meal from the solvent contains only 1 per cent. of oil. This mixed process is largely worked on the Continent.

Copra.—This material is the flesh of the cocoa-nut. It is usually pressed twice owing to the difficulty of making cakes when pressed only once (unless very powerful presses are employed) and also on account of the very large amount of oil it contains. The copra is passed over a magnetic machine to remove all pieces of iron, smashed up in disintegrators, crushed in Anglo-American rolls, and automatically conveyed to the kettle or heater of the presses, which may be either "Anglo-American" or "cage" type, for the first pressing. Usually the material is worked cold the first time, the resulting cakes being ground up and heated for a final pressing. This process, with slight deviations, is used for treating all very oily seeds, such as ground nuts (Arachides), palm kernels, sesame, copra, etc.

(*b*) Extraction of Oils and Fats by Means of Volatile Solvents

The oil cakes obtained by the pressing process may contain anything betw 7 and 10 per cent. of oil. Such cakes are often sold as a valuable cattle f Occasionally, however, when larger quantities of oils and fats than can be obta by pressing are desired, the rest of the oil is extracted by solvents, which ca easily made to remove all except, perhaps, 1 per cent. Bones are extracted the same manner.

On the large scale three solvents are employed, viz., carbon disulphide, petroleum e (benzine), and carbon tetrachloride.

Chloroform and **Ether**, although excellent solvents, are at present too dear to employ extracting on the large scale.

Carbon disulphide, CS_2, boils at 46° C. and has a sp. gr. of 1.293. It is a colourl liquid and smells something like chloroform. When impure, however, it contains evil-smell sulphur compounds, from which it may be purified by distilling first over sodium carbonate and t over freshly pressed plant oils, which retain these impurities almost completely. Carbon disulph easily inflames and so is a dangerous substance. Its vapour sometimes catches fire when in cont with hot metallic surfaces heated to about 150° C., so that a violent explosion can be caused mer by a hot steam pipe or bearing heated by friction.

With **Petroleum ether**, boiling between 80°-120° C., the danger of inflammation is much and at the same time it is cheaper. It is, therefore, gradually replacing carbon disulphide. Carb disulphide, however, is the better solvent, resinous fats and old palm oil being much more solu in it than in petroleum.

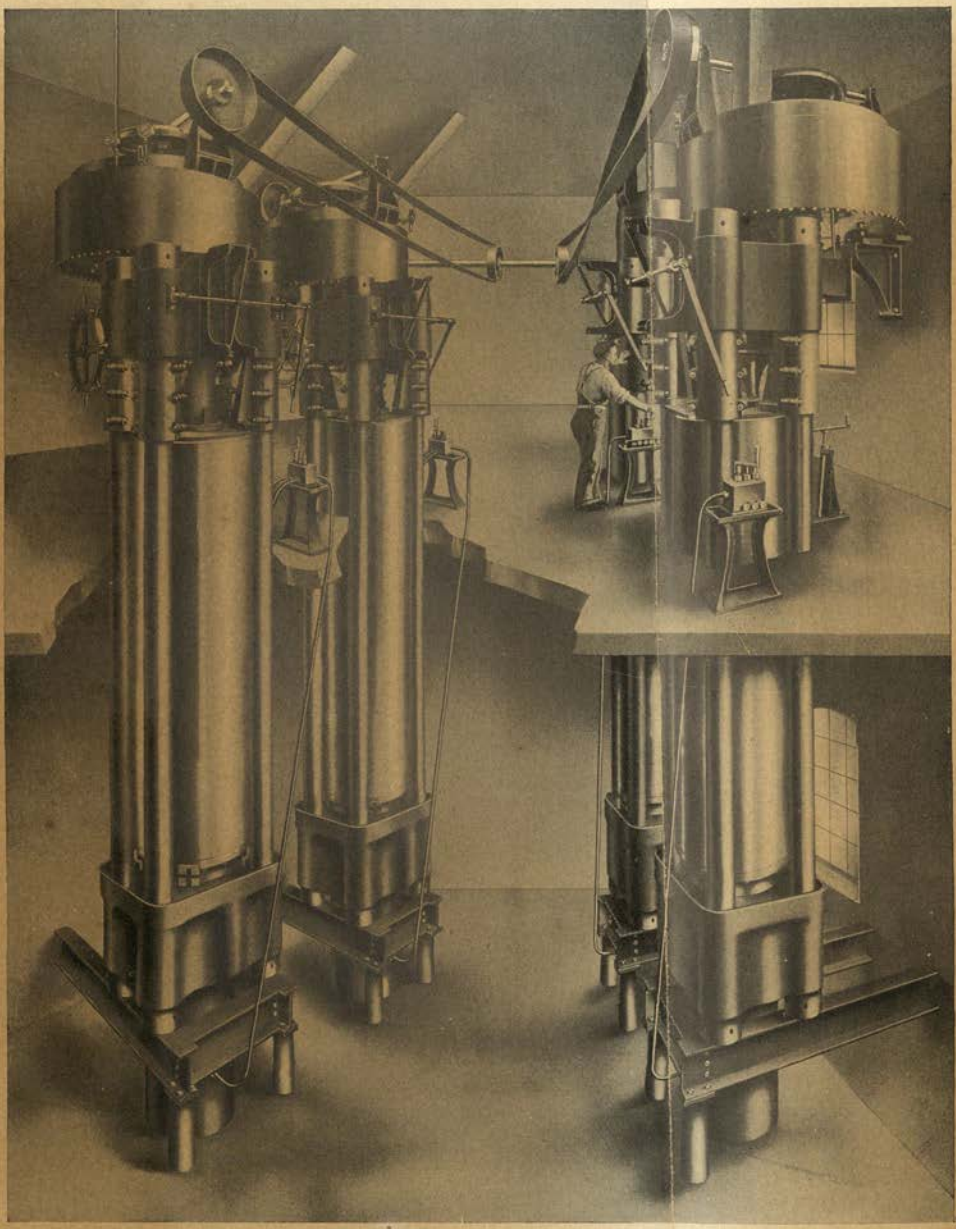

FIG. 11.—IMMENSE PRESSES USED FOR EXPRESSING CASTOR OIL FROM CASTOR SEED.
(Rose, Downs, & Thompson Ltd., Hull.)

[*To face page* 30.

Carbon tetrachloride, CCl_4, is a good solvent, being easily volatile (B.P. 76.5° C., sp. gr. 1.582) and non-inflammable. It is being employed for extracting bones and fats, the products obtained having a good colour; the odour of the tetrachloride can be completely expelled by blowing steam through the oil. Oils extracted by petroleum spirit always retain its smell. The main disadvantage that carbon tetrachloride suffers from is its great weight (sp. gr. 1.582), its dearness, and the fact that it attacks metal work. It must be noted that both carbon disulphide and carbon tetrachloride exert a poisonous physiological action, whereas petroleum spirit is not poisonous enough to affect the workmen.

Two methods of extraction are employed:—

1. Extraction by cold solvents.
2. Extraction by hot solvents.

1. Cold Extraction.—This is preferable as regards fire insurance and is largely practised with carbon disulphide for obtaining palm fats out of palm kernels.

The crushed and warmed seeds are charged into A (Fig. 12) (one of a battery of six closed iron cylinders) on to a perforated bottom F covered with sackcloth, and a stream of carbon disulphide from a reservoir is allowed to percolate through, passing in by B and flowing away by L (which is provided with a strainer) into the next cylinder of the series. The solvent thus flows through each cylinder in order, from the top to the bottom, remaining for a short time in each before passing on into the next. The solvent leaves the battery charged with about 50 per cent. of fat. The exhausted cylinders are heated by a current of steam passed in through C, and the solvent still in the seeds is driven off through D, condensed in long tubes, and used again. The solvent containing the fats is pumped to the steam-heated still R, where the solvent is boiled off by the steam coils J K (Fig. 13). The vapours rise through M and the solvent is recovered by condensing the former in a special condenser. The residue of oil or fat left in R is freed from ent by blowing steam through it, which the oil is run off through P allowed to stand until the condensed r has separated out. The battery of els is so constructed that any one can made the last of the series ready to discharged and refilled with fresh meal, so that the process is a practically tinuous one, the only time lost being in the actual refilling and discharging, ch is effected by removing the clamped-down cover from A.

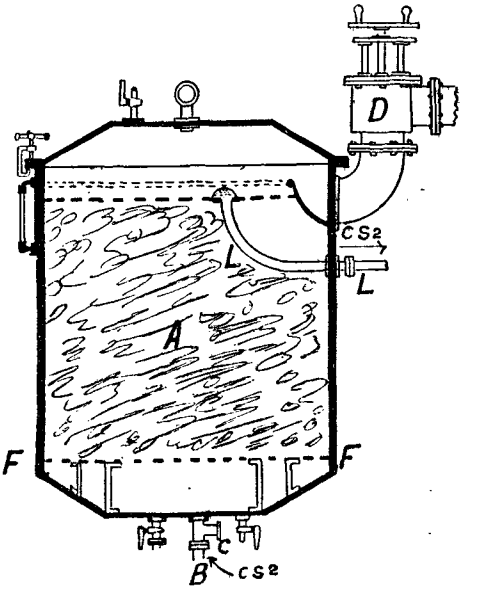

FIG. 12.—Cold Extraction Plant.

The loss of solvent amounts to only 0.5 per cent. to 1 per cent. on 100 parts of The fat is digested with a little concentrated sulphuric acid, and drawn off o wooden vessels. Fat obtained from carbon disulphide extraction is nearly ourless, whereas that obtained by this process from benzine still retains a slight ur of this solvent and may be used for making soap.

2. Hot Extraction.—In this process the extraction takes place continuously h a limited amount of solvent charged once for all into the apparatus, which is rely an enlarged form of the Soxhlet extractor employed in the laboratory.

An apparatus extensively used for extracting fat from bones by means of benzine illustrated below.

The degreasing boilers A, A (Fig. 14) are filled with air-dried bones which rest on the rforated floor *n n*. The lower space B is heated by means of a steam coil *d*. By

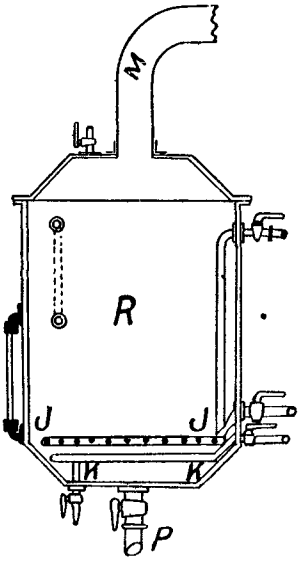

FIG. 13.—Still for Cold Extraction Plant.

means of a nozzle *b* live steam can be blown in. Benzine is heated in the boiler C by means of a steam coil, and the benzine vapour, rising upwards, is superheated to 120°-130° C. in the tubular superheater D by means of high-pressure steam. The superheated benzine vapour issues from small holes in the tube *r* and streams upwards through the bones. Part of the vapour condenses here, and flows down, carrying with it fat extracted from the bones, and collects in B, where it is continually boiled by means of the steam coil *d*. Part of the benzine vapour escapes in the gaseous state through *p*, and, together with the water simultaneously expelled from the bones, is condensed in the cooler E. The superheating of the benzine vapour is necessary in order to dry the bones and thus enable the solvent to more thoroughly penetrate them. When no more water passes over the process is complete. A current of live steam is then blown through the apparatus by means of the nozzle *b*, and this soon drives the benzine out of the fat in B as well as that still remaining in the bones in A. The benzine thus expelled, together with condensed steam, collects in the water-separator F. The benzine being lighter than the water, collects on the surface and flows continually out at *g* into the benzine reservoir *g*, the water flowing away by *w*. From the reservoir *g* the benzine flows into the lower-situated vessel C and is used over again.

It will be seen that very little benzine is necessary to effect extraction, the same benzine being used over and over again. Bones treated thus yield 6-7 per cent. of fat.

A typical modern extraction plant for scents is described on p. 134.

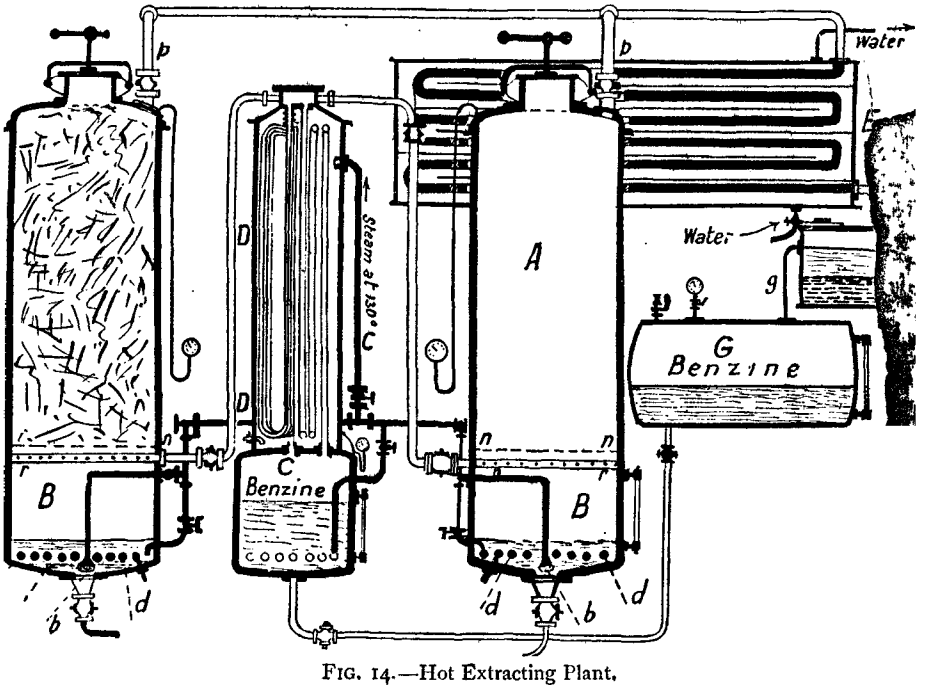

FIG. 14.—Hot Extracting Plant.

Merits and Demerits of the Methods of Extracting Oils and Fats by Pressure and by Solvents

1. Edible oils and fats cannot at present be prepared by extraction by solvents, since enough solvent is always retained to impart a nauseous taste. Such oils and fats are, therefore, only used for soap-making and other technical purposes.

2. Extracted meal by itself is not suitable for feeding cattle. On the Continent it is mixed with press cake and sold for this purpose. Press cake is, however, far better as a food material from a stock-raising point of view than the cakes obtained by the extractive process, even when these latter have oil or fat added to them so as to equal the proportion contained in the pressed cakes.

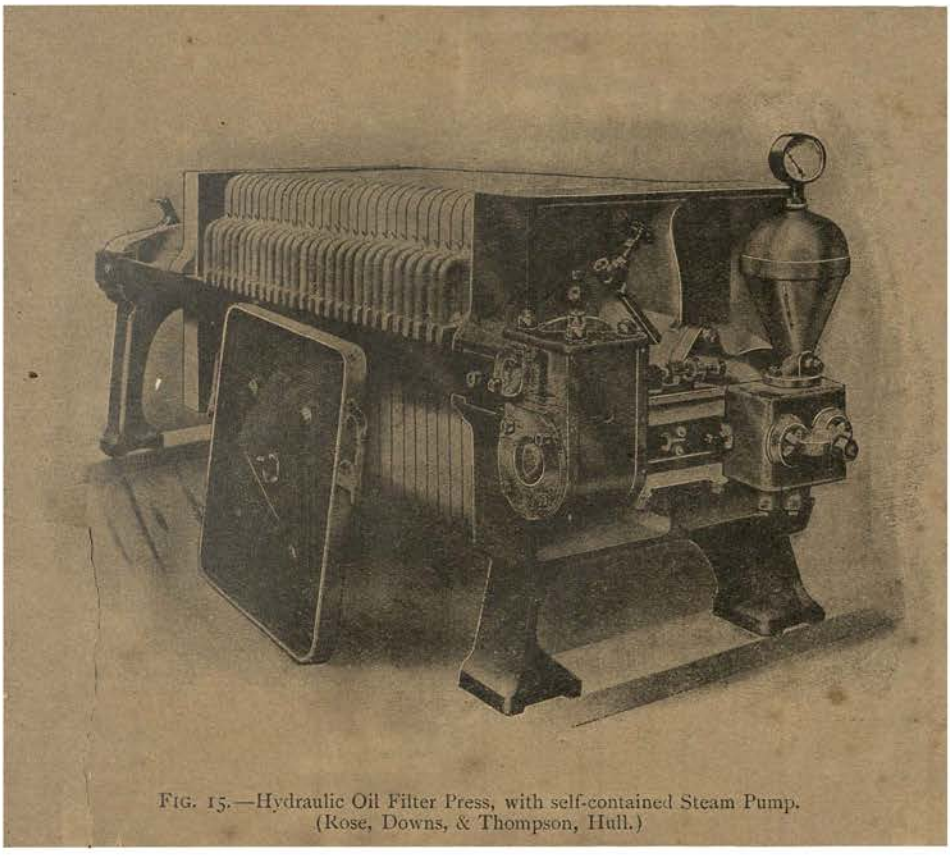

FIG. 15.—Hydraulic Oil Filter Press, with self-contained Steam Pump. (Rose, Downs, & Thompson, Hull.)

3. The solvent process extracts the fats and oils to a far larger extent than the pressure process, only about 1 per cent. of oil being left in the extracted seed, against 7-10 per cent. in the pressed. In many cases a combination of pressure and solvent processes is the best, oil being first expressed and sold as edible oil, and the residue, still fairly rich in oil, is extracted, and the oil thus obtained sold for soap-making and other technical purposes.

General Methods of Refining and Bleaching Oils and Fats

The actual process adopted depends somewhat upon the nature of the oils. If these are fresh and well made, they may be worked up directly into technical products without any refining.

(*a*) **Tanking and Filtering.**—The oils are run into tanks and allowed to stand. Dirt and impurities settle to the bottom, and the supernatant oil becomes clear Sometimes oils are tanked for months or years at a time (*e.g.*, linseed oil).

A much quicker process is direct filtration, which avoids the loss of time and storage space necessitated by the old plan of subsidence, the sole product of the oil mill being a cake and bright oil, the residue in the filter being worked back again in the mill. The filtration is effected by pumping the oil direct from the hydraulic presses through a filter press (Fig. 15). This consists of a series of grooved iron plates, hollow on the inside, which are clamped tightly together, and which contain cloth separating them. The oil is thus forced through a succession of cloth filters, and the solid matters are caught and deposited in the spaces between the cloths.

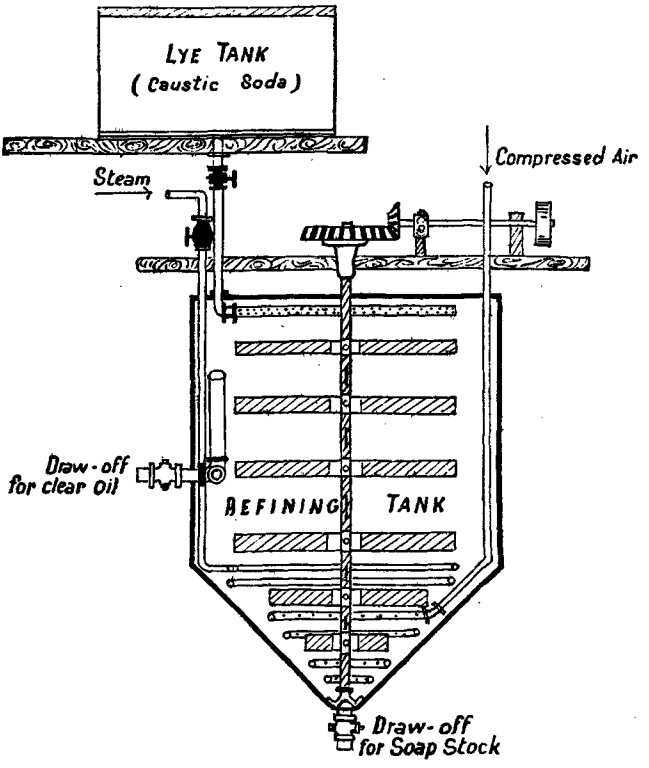

FIG. 16.—Cotton-Seed Oil Refining Tank.

Nothing but oil comes in contact with the plates, the oil passing out at the end pure and bright.

(*b*) **Treatment with Caustic Soda or Sulphuric Acid.**—The oil is washed in special tanks with a solution of caustic soda or sulphuric acid. Thus *cotton-seed oil* is pumped into a large tank of the construction shown, then heated by steam to 30° C., and the proper amount (which depends upon the quality of the oil) of caustic soda solution (74° Be.) run in and mixed thoroughly either by mechanical agitators, or by a current of air blown through the liquids for fifteen minutes. On standing, a sediment of coagulated albuminous and mucilaginous matter from the oil settles at the bottom of the tank together with the excess of caustic soda solution. The oil is cooled and siphoned off from the sediment to

a finishing kettle, where it is washed free from caustic soda by a stream of water. The wash water is withdrawn from the bottom of the kettle until oil comes; then fresh water is added, and the process repeated until the oil is free from alkali. During this operation a blast of air is blown through the liquids, or mechanical agitators are used, in order to thoroughly mix the oil and water.

Finally moisture is expelled by heating the oil gently by steam pipes to a temperature not higher than 50° C., while a current of air is blown through. The last traces of moisture are sometimes removed by adding plaster of Paris and filtering. Filtration through a layer of common salt also removes all moisture.

Many industrial oils are purified as above, but with a solution of *sulphuric acid.* About 2 per cent. of sulphuric acid of 66° Be. mixed with an equal volume of water, is run into the oil contained in a lead-lined tank; then the liquid is agitated by an air blast, warmed for about one hour, settled, the acid run off at the bottom, and the oil washed with water and caustic soda until free from acid; finally the clear supernatant oil is decanted and filtered.

Edible oils and oils for lubricating purposes are nearly always purified with caustic soda, which removes the nauseous tasting free fatty acids. A trace of mineral acid spoils the oil for lubricating purposes.

Deodorisation of Edible Fats.—Certain high-grade edible fats and oils are sometimes extracted with alcohol. They are stated to be rendered perfectly odourless and tasteless by this process, and so can be employed in the manufacture of high-class margarine and similar comestible fatty products.

Two methods are well known for the deodorisation of cocoanut oil:—(1) **Washing out the odoriferous bodies with alcohol.** This removes the fatty acids, and also such substances as phytosterol. *Chevreul* and *Schlinck* employ a joint process of washing with alcohol followed by treatment with charcoal. For a recent patent see **Urbain** and **Friegé** (French Patent, 361,966, 1905). (2) **Volatilisation by steaming.** Jeserich and Meinert (1882) passed high-pressure steam at 6-8 atmospheres into the fluid oil for two to three hours; the non-volatile fatty acids left were then removed by adding 0.25 per cent. of calcined magnesia, and the magnesium soap formed is then skimmed off the surface. Klimont (English Patent, 3,164, 1902) neutralises the oil with alkali before treating with steam.

(*c*) **Bleaching with Chemicals.**—Actual bleaching with chemicals is only resorted to in the case of inferior or very dark oils and fats. Bleaching by means of oxygen in a nascent state is usually effected by adding manganese dioxide or potassium bichromate and sulphuric acid:—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$
$$K_2Cr_2O_7 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$$

Sometimes bleaching powder or potassium bichromate, together with hydrochloric acid, is used, when chlorine is evolved, thus:—

$$Ca(ClO)_2 + 4HCl = CaCl_2 + 2H_2O + 4Cl$$
$$K_2Cr_2O_7 + 14HCl = 2CrCl_3 + 2KCl + 7H_2O + 6Cl$$

No general rule can be given as to the best process to employ in a given case; thus *tallow* is usually bleached with manganese dioxide and sulphuric acid, while *palm oil* with bichromate and hydrochloric acid. The quantity of chemicals employed must be as small as possible, the time of interaction as short as possible, and the temperature as low as is compatible with efficiency. The glycerides may be seriously damaged if such conditions are not rigorously observed.

It will be sufficient if we describe the Sulphuric Acid Bichromate Oxidation Process. The melted oil or fat at a temperature of about 38° C. is pumped into a lead-lined chemical treatment tank, compressed air is blown through it in order to thoroughly mix the contents, while the requisite amount of bichromate solution (1 bichromate : 4 water by weight) is run in. The mixing is continued for about one hour while the contents of the tank are simultaneously warmed by a steam coil. Finally the liquid is allowed to settle, the acid run off at the bottom, and the oil washed with water to remove acid.

Palm Oil is now bleached on quite a large scale by means of oxygen, and more recently, by ozone. An apparatus for bleaching palm oil by atmospheric oxygen is represented in Fig. 17. A closed vessel is fitted at A with a steam jet exhauster, and a copper heating coil K K. At the bottom of the vessel is an annular air-distributing pipe with a large number of small holes connected to an inlet pipe carrying compressed air, oxygen, or ozonised oxygen.

The palm oil, which has been previously liquefied, and allowed to stand so that the water and dirt may settle to the bottom, is run into the iron vessel, heated by the steam coil to 100° C., and air is blown through. The oxygen removes most of the colouring matter, and as in this process no strong chemicals are used, the natural properties of the oil are not affected. The process may take two hours. Rank fish oils are deodorised and decolourised by this process. Sometimes instead of air steam at a temperature of 110° C. is driven through the oil, ten hours' steaming being sufficient to deodorise 4 tons of oil. Another method of bleaching palm oil (and which yields good results with almost all other kinds of oils) is this: Melt, say, 100 parts of palm oil in a boiler, and when liquid add a solution of chloride of lime, made by dissolving 7 parts by weight of the chloride in water for every 84 parts by weight of oil; mix intimately, cool, and cut the hardened mass into small pieces, and leave exposed to the air for a few weeks. Next place the fat in a boiler lined with lead, add a 5 per cent. solution of sulphuric acid, equivalent in total amount to the lime chloride, heat, separate the oil from the acid, wash, and allow to solidify.

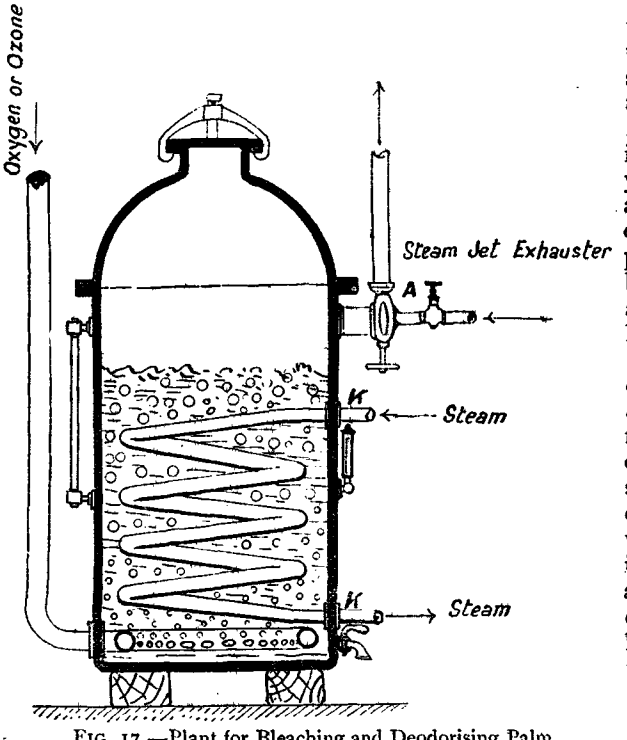

FIG. 17.—Plant for Bleaching and Deodorising Palm Oil by means of Oxygen or Ozone.

Bone Fat is often bleached as follows: place the fat (which must be free from gelatine and calcium phosphate) in an iron pan, add an equal weight of brine of 14°-15° Be., boil for three hours, allow to stand twelve hours, draw off the fat into a wooden vessel, and treat with a mixture of 2 parts potassium bichromate dissolved in boiling water, and 8 parts of hydrochloric acid (22° Be). This quantity is sufficient for 400 parts of fat. Leave the mass standing, stirring at intervals, when decoloration proceeds gradually. When complete, wash the fat with hot water.

Linseed Oil may be refined by placing 236 gallons into a copper boiler, adding 6 lbs. of oil of vitriol, and stirring together for three hours. Next add 6 lbs. of fuller's earth mixed with 14 lbs. of hot lime, stir three hours, run off the oil into a copper vessel containing an equal volume of water, boil three hours, draw the fire, and when the oil is cold, run off the water and let the mixture settle for some weeks.

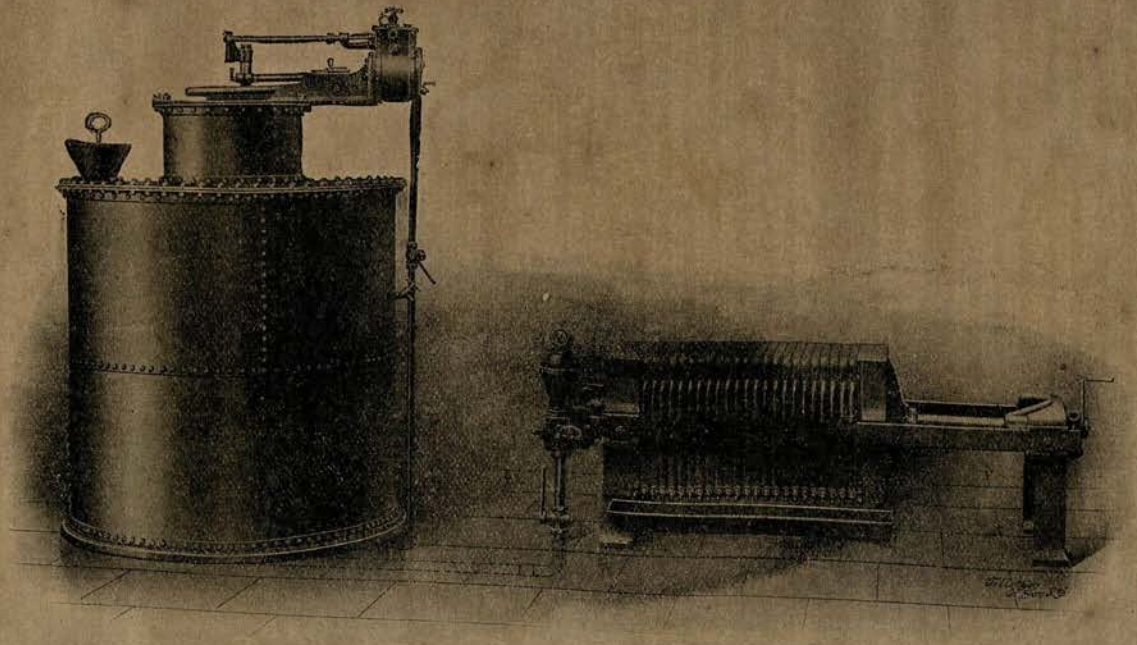

FIG. 18.—Fuller's Earth Plant. For treating lard, cotton-seed oil, cocoanut oil, ground-nut oil, etc.
(Rose, Downs, & Thompson, Hull.)

It is frequently decolourised by a 30 per cent. solution of $FeSO_4$ or with KOH followed by $K_2Cr_2O_7$ and HCl. Other ways used are:—

1. *Sun Bleaching*, employed for the most expensive varieties of artists' oil. The oil is exposed to sunlight in shallow trays under glass.

2. *By Hydrogen Peroxide.*—Shake the oil in a glass bottle with a 5 per cent. solution of hydrogen peroxide, and allow to stand for some days, shaking occasionally. The oil clarifies and is poured off from the water at the bottom.

3. *By Potassium Permanganate* (suitable also for poppy oil).—Place 25,000 parts of oil in a large glass balloon, add a solution of 50 parts of potassium permanganate in 1,250 of water, stir well, allow to stand twenty-four hours at a gentle warmth, then add 75 parts by weight of powdered sodium sulphite, agitate well, add 100 parts of hydrochloric acid, again agitate, and allow to stand until decolourisation takes place. Wash the oil with water rendered milky with chalk powder until free from acid, and finally separate the water, and filter off the oil through anhydrous sodium sulphate.

Bleaching of linseed oil with chloride of lime and hydrochloric acid, or calcium bichromate and sulphuric acid, is sometimes employed, but the operation requires great care and is sometimes dangerous.

Decolourisation with Fuller's Earth, Animal Charcoal, etc.—Animal charcoal is by far the best decolourising (and deodorising) agent known, yet on account of its cost it can only be employed for edible oils and fats. More usually fuller's earth or powdered kaolin is used, being less expensive than charcoal. The oil is treated with the decolourising powder in a special mixer. The apparatus shown in Fig. 18, p. 37, is that manufactured by Rose, Downs, & Thompson at Hull. It consists of a steam-jacketed cylindrical steel tank with a contracted neck at the top, and provided with a powerful stirring apparatus for rapidly mixing the fuller's earth with the oil. The tank is filled to the underneath part of the neck with the oil or fat to be treated (which has been previously heated to 40°-60° C.), and 3-5 per cent. of fuller's earth (the exact quantity depending upon the amount of colour to be removed) rapidly stirred in. The earth should be in the form of a perfectly dry powder. It is a silicate of aluminium.

Oils and lard, which are to be used as food, must not be left in contact with the fuller's earth for more than fifteen minutes after mixing or they begin to acquire an earthy flavour. Consequently the materials must be separated as rapidly as possible after they have been stirred round for the right time.

The oil or lard is rapidly pumped away through the filter press, which retains the fuller's earth, the oil passing on through the filter cloths. Finally steam is blown through the press so as to free the cakes from oil. When the press is opened the earth falls out as a powder upon the floor, little or no oil being left in it. When dealing with fats or waxes which are solid at ordinary temperatures (*e.g.*, tallow, lard, paraffin wax) the filters are steam-jacketed so that their contents can be maintained at any temperature necessary to prevent the solidification of the fat in the presses.

Demargination of Oils.—Many of the vegetable oils (such as cotton-seed, arachis, fish, and some sorts of olive oil) deposit a crystalline mass of "stearin" on standing. It is very important that edible oils should not solidify at temperatures near the freezing point. Also lubricating oils must necessarily remain liquid at low temperatures, an oil still fluid at $-15°$ C. being demanded for railways in the United States. Such oils are known as "Winter Oils."

Hence many natural oils must be "demarginated" before they can be placed on the market. Originally the process consisted in simply storing the oil in large vessels through the winter, when the "stearine" separated out as a white solid mass at the bottom. The supernatant oil, when drawn off, formed the "winter oil." This process is still used for arachis oil, but in other cases the cooling is artificially carried out, and the stearine removed by forcing the oil through a filter press.

Fig. 19 shows an oil-cooling and filtering plant designed by Rose, Downs, & Thompson, of Hull. The oil is placed in the tank C, which is provided with agitators and a cooling coil. The cooling effect is produced by allowing anhydrous ammonia, condensed to a liquid by the pump B, to expand through the cooling coil in the tank C. Here the liquid suddenly expands into a gas, producing intense cold in so doing. The oil, under the influence of this cold, and aided by a vigorous mechanical stirring, deposits its stearine in the solid form at the bottom of the tank. The ammonia, now issuing as a gas from the cooling coil, is recondensed to a liquid by the pump B, the compression being carried out in the tank C, filled with cold water, which effectively carries away the heat generated in the operation. The process is continued until the oil is reduced to the temperature at which it is desired to remove the stearine. When this point is reached the oil is drawn off and pumped through the filter press D, which removes any suspended stearine crystals.

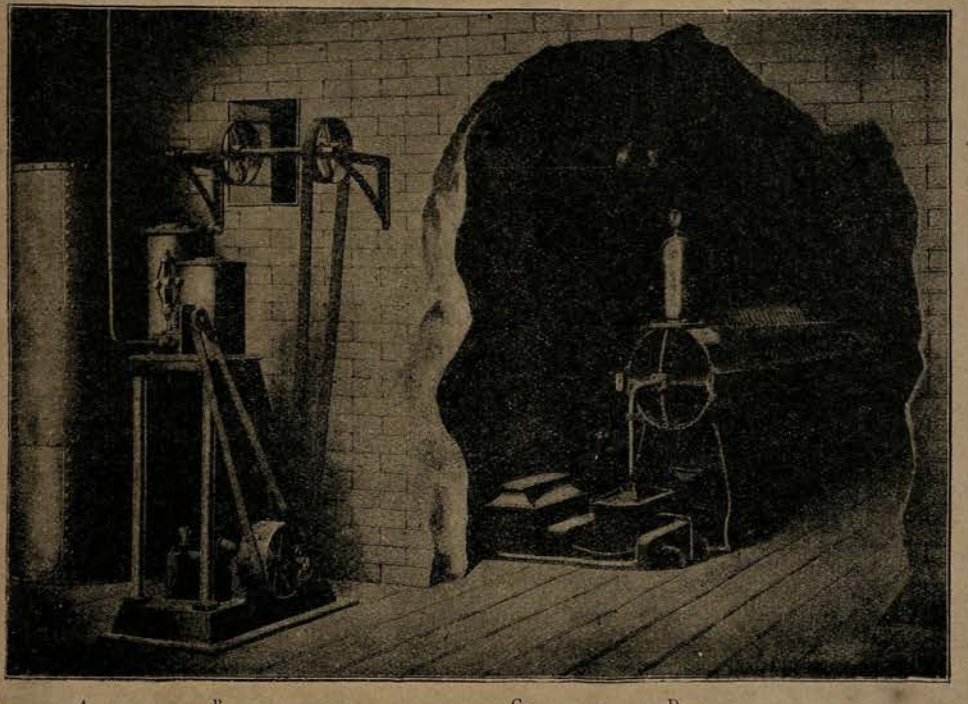

FIG. 19.—Oil-Cooling and Filtering Plant, for the separation of stearin and olein. (Rose, Downs, & Thompson, of Hull, England.)

Oil which has been treated in this way will always remain clear and bright at any temperature above that at which the stearine has been removed.

The separated stearine is a valuable product, being largely used for making margarine, margarine cheese, lard substitute, etc. etc.

VARIETIES OF FATS, FATTY OILS, AND WAXES

Classification

For convenient description we divide the oils and fats under the headings: (1) Animal fats and oils, (2) Vegetable fats and oils, (3) Waxes.

1. **Animal Fats and Oils.** These include **Fish Oils.**—The oils derived from marine animals are characterised by their odours and, analytically, by a high Maumené and iodine value.

2. **Vegetable Fats and Oils** may be conveniently arranged, according to their iodine values, into (*a*) **Solid fats,** (*b*) **Non-drying oils,** (*c*) **Semi-drying oils,** (*d*) **Drying oils.**

No rigid line can be drawn between these classes, as they merge into each other. The iodine value affords a means of ascertaining roughly their constitution and gives a rough basis of classification. Triolein has an iodine value of 86.2 and consequently if an oil absorbs more than 86.2 per cent. of iodine it probably contains the glyceride of an acid of the linolic or linolenic series. Now linolic and linolenic acids and their glycerides readily absorb oxygen from the air—a property not possessed by oleic acid and triolein—and it is due to the presence of **trilinolin** and **trilinolenin** that the drying oils owe their property of drying by absorbing of oxygen on exposure to air. Since the iodine value of pure trilinolin is 173.6, oils having an iodine value of above 170 may be classified as **drying oils**; those having an **iodine value** of 90 or lower may be called **non-drying oils**; while oils having intermediate iodine values may be called **semi-drying.** In practice it is found that **oils** with iodine values above **140** have valuable drying properties; those with iodine values 100-140 are semi-drying, since they are able to absorb a certain quantity of oxygen, but will not dry completely when exposed to the air in a thin layer. Oils with iodine values less than 100 are practically without drying value.

The **Fish oils** form an exception to this rule; some of them have iodine values as high as that of linseed oil and absorb large quantities of oxygen; yet they do not usually dry to a hard layer. Their unsaturated acids are of a different constitution from linolic and linolenic acids.

3. **The Solid Waxes of Animal and Vegetable Origin,** and the liquid waxes (sperm oil, bottlenose oil) are characterised by their high content of higher alcohols (unsaponifiable matter). They do not contain glycerol. They are therefore treated as a separate class under the title of **Waxes** (see p. 52).

Varieties of Animal Fats and Fatty Oils

Tallow, the solid fat of oxen and sheep, consists of tristearin, tripalmitin, and 40-46 per cent. triolein.* Mutton tallow melts 45°-55°; oxen tallow 45°-50° C.; solid point, 40°-47°; Reichert value, 0.25; Hehner value, 96; iodine value, 35-46; saponification value, 193-198; sp. gr. 0.86 at 100°, 0.94-0.95 at 15°. Melting point of fatty acids, 38°-49° C.; solid point, 38°-48°.

Tallow Oil.—Very similar constants to lard oil; iod. val. = 32-57; Maumené, 41°-44° C.

Lard is the rendered fat of pigs. American lard often contains cotton-seed oil and tallow.—M.P. 30°-49°; sol. pt. 23°-30°; sap. val. 195-197; iod. val. 50-77; Hehner val. 95-98; sp. gr. (100° C.) 0.860-0.864. The separated fatty acids have sol. pt. 34°-42°; mol. wt. 278; iod. val. 64; refract. index, 1.439 (60° C.).

Lard Oil, Oleo Oil.—Acid val. 0.4; sap. val. 193; Hehner val. 97.4; Reichert-Meissl val. 0.4-0.9; iod. val. 53-88. Insol. fatty acids have sap. val. = 206.

Goose Fat.—M.P. 25°-34°; sol. pt. 18°-20°; sap. val. 184-198; iod. val. 60-72; Reichert-Meissl val. 0.2-0.3; Hehner val. 92-96; sp. gr. 0.91-0.93.

Butter Fat is described under Butter.

* Recent researches have shown the presence of mixed glycerides.

Bone Fat, from fresh bones.—M.P. 21°-22°; sol. pt. 15°-17° C.; sap. val. 190-195; iod. val. 46-56; sp. gr. 0.914-0.916 at 15° C. **Mixed fatty acids**, M.P. 30°; sol. pt. 28°; neut. val. 200; iod. val. 56-58. Fat extracted from old bones by benzine is dark, smells unpleasantly, contains calcium soap (derived from mineral matter of bones) and free fatty acids. Used for soap-making.

Sheep's Foot Oil, Horse Foot Oil, and Neat's Foot Oil are yellowish oils valuable for lubricating (since they do not easily become rancid), obtained by boiling the feet of cattle with water.—Sp. gr. 0.91-0.92 at 15° C.; sap. val. 194-197; iod. val. 73-75; Maumené test, 38°-50° C. Mixed fatty acids, sol. pt. 20°-26° C.; iod. val. 66-76; neut. val. 200-206.

Horse Fat, yellowish, often becomes rancid.—Sp. gr. 0.89-0.93 at 15° C., 0.79-80 at 100° C.; M.P. 40°-50°; sol. pt. 22°-48°; iod. val. 75-85; Reichert val. 0.33; Hehner val. 95. Mixed fatty acids, M.P. 36°-41°; sol. pt. 30°-33°; iod. val. 74-84.

Fish Oils are usually fluid, containing glycerides of oleic, stearic, physetolic acids, and other unsaturated acids. Unless of the best medicinal qualities these oils are dark, evil-smelling fluids in consequence of small quantities of decomposition products of decaying fish (trimethylamine).—Sp. gr. 0.92-0.933; sap. val. 170-200; iod. val. 100-110; Reichert val. 1.5-2.2; Hehner val. 95; Maumené's test, 100°-128° C. Mixed fatty acids, sol. pt. 21°-28°.

Fish oils are now used both in the ordinary and the enamel leather trade with excellent results; and the enamel leather produced, whilst not quite so glossy as when linseed oil is used, is said to be more flexible and less liable to crack; also for soap-making, and in the manufacture of printing ink.

When cooled, fish oils often deposit solid masses of **Fish Stearine** (fish tallow).

Sod Oil (Dégras) is the waste oil obtained in the process of chamoising leather. The leather is soaked in fish oils and then exposed to the air. Oxidative and fermentative processes set in which convert the contained oil into sod oil. The oil is extracted from the leather by means of sodium carbonate solution, and then separated from the emulsion it thus forms by the addition of dilute sulphuric acid. A similar product is obtained by blowing air through fish oils heated to 120° C. Sod oil consists principally of unchanged fish oil, owing its valuable properties to the presence of a resinous acid "dégras former," of unknown constitution, soluble in alkalies, insoluble in petroleum ether; it is this substance which makes sod oil so suitable for oiling dressed leather.—Sp. gr. 0.92-0.98 at 15° C.; refract. index, 1.475-1.478; acid val. 8-28; sap. val. 180-190 (from shark liver oil only, 143); acetyl val. 22-48; iod. val. 70-100.

Varieties of Vegetable Fats and Oils

(*a*) SOLID VEGETABLE FATS (*i.e.*, M.P. above 20° C.)

Cacao Butter is expressed from cacao beans in the process of working them into cacao.—M.P. 30°-34°; sap. val. 192-200; iod. val. 34-37; Reichert-Meissl val. 0.83; refract. index (60° C.), 1.45. Sp. gr. 0.96-0.97 at 15°, 0.85-0.86 at 100°. The insol. acids have M.P. 48°-53°; neut. val. 190; iod. val. 32-39; refract. index, 1.42 (60° C.).

Chocolate Fats.—The best substitutes for cacao butter are made by expressing, at a temperature slightly over the normal atmospheric temperature, the solid fats which crystallise out from palm-nut and cocoa nut oils. Small quantities of animal fats are sometimes added to raise their melting points; these, however, sometimes impart an unpleasant taste, and it is better to use for the purpose vegetable fats such as those from margosa or mowra oil. Sap. val. 242-254; iod. val. 6-10; M.P. 25°-30°; Reichert-Meissl, 3.5-8.0.

Nutmeg Butter is obtained from the seeds of *Myristica officinalis*.—Sp. gr. 0.94-99 at 15°, 0.88-90 at 100°; M.P. 38°-50° C.; acid val., 22; sap. val. 156; iod. val. 40-80.

Chinese Vegetable Tallow is the hard fat which coats the seeds of the Chinese tallow tree.—M.P. 44°-53° C.; sap. val. 200; iod. val. 32.

Japan Tallow is a similar fat which surrounds the berries of certain sumach trees which flourish in China and Japan; rich in palmitin.—M.P. 50°-53°; sap. val. 220; iod. val. 4-15.

Palm Oil, obtained in very large quantities from the fleshy parts of the fruit of certain palm trees, is a fat having a sweetish taste and an odour resembling that of violets, which persists even after bleaching with air at high temperatures, and after making into soap. It consists principally of tripalmitin, triolein, and free fatty acids; the proportion of the latter is sometimes very large in commercial specimens owing to a process of enzyme hydrolysis which goes on in the shipped oil.—Sp. gr. 0.92 at 15° C., 0.85 at 100° C.; sol. pt. 31°-38°; M.P. 27°-42° C.; sap. val. 202; iod. val. 51-57; Reichert-Meissl val. 0.9; Hehner val. 95; refract. index (60° C.) 1.451. Insol. fatty acids have sol. pt. 36°-45°; M.P. 47°-50°; neut. val. 204-206; iod. val. 53.

Palm-kernel Oil, Palm-nut Oil is obtained from the kernels of the palm tree fruit, and contains much lauric acid. It is easily saponified by cold concentrated caustic soda solution.—Sp. gr. 0.91 at 40°, 0.87 at 100° C.; sol. pt. 23° C.; M.P. 23°-30° C.; sap. val. 250; iod. val. 10-17; Reichert-Meissl val. 5-7; Hehner val. 91; refract. index (60° C.) 1.4431. Insol. fatty acids have sol. pt. 20°-25°; neut. val. 251-265; iod. val. 12.

Cocoa-nut Oil is the fat obtained from the kernels of the cocoa-nut. The fleshy part of the kernel, called copra, contains a large amount of fat, which consists of glycerides of lauric, myristic, palmitic, and other acids, some of them volatile. The fat, like palm-kernel oil, is easily saponifiable in the cold by concentrated caustic soda solution. Largely used for soap and margarine manufacture. For the latter purpose it is deodorised (1) by washing with alcohol, or (2) by treating with superheated steam (see p. 35).—Sp. gr. 0.92 at 15°, 0.86-0.90 at 100° C.; sol. pt. 16°-23° C.; M.P. 23°-26°; sap. val. 250-260; iod. val. 8-9; Reichert-Meissl val. 7-8; refract. index, 1.43 (60° C.). The fatty acids have sol. pt. 20°-25°; neut. val. 258; iod. val. 8-9.

Mahwa Butter, Mohwrah Butter, Mohrah Seed Oil (from *Bassia latifolia*).—M.P. 23°-29°; acid val. 5-71; sap. val. 187-194; Hehner val. 95; Reichert-Meissl val. 0.4-1.0; iod. val. 50-68. Insol. fatty acids, sap. val. 206.

Mowrah Seed Oil (from *Bassia longifolia*).—Sap. val. 196-202; iod. val. 50.

Myrtle Wax.—Acid val. 3; sap. val. 205-212; iod. val. 1.9-4. **Fatty acids** have neut. val. *c.* 230.

Shea Butter, Bambuk Butter, Karité Oil, from the seeds of *Bassia Parkii* (West Africa and Soudan).—Sp. gr. 0.85-0-92 (15° C.); M.P. 25°-28° C.; sol. pt. 17°-18°; sap. val. 171-192; iod. val. 56-59.

(*b*) Liquid Vegetable Non-Drying Oils

These do not absorb oxygen from the air, nor do they dry up. Iodine value usually under 100.

Olive Oil, much valued as an edible oil (salad oil), is obtained from the fruit of the olive tree. The cold pressed oil is the best; the second pressings or the

oil extracted by carbon disulphide is used for soap-making; consists of 70 per cent. triolein, 28 per cent. tripalmitin and tristearin, and a little linolein.—Sp. gr. 0.914-0.918; sol. pt. 2°-4° C.; sap. val. 190-195; iod. val. 79-93; Reichert-Meissl val. 0.6; Hehner val. 95; Maumené test, 41°-47° C.; refract. index, 1.47 (15° C.); viscosity, 312 secs. at 21° C. The fatty acids have sol. pt. 17°-26°; neut. val. 193; iod. val. 86-90.

Olive-kernel Oil.—Acid val. 2-3.5; sap. val. 182-188; iod. val. 79-88.

Almond Oil, obtained from bitter and sweet almonds, is very similar to **Peach-kernel Oil, Plum-kernel Oil,** etc.—Sap. val. 190-195; iod. val. 93-100.

Arachis Oil, Pea-nut Oil, Earth-nut Oil, is an edible oil obtained from the seeds of *Arachis hypogæa*. It contains arachidic acid as a glyceride.—Sap. val. 190-196; iod. val. 90-103; Reichert-Meissl val. 0.5; Maumené, 45°-75°; viscosity, 300-430 secs. at 21° C.; refract. index (15° C.) 1.47. The insol. fatty acids have sol. pt. 23°-28°; neut. val. 202; iod. val. 96-105.

Croton Oil.—Sap. val. 210-215; Reichert-Meissl val. 12-14; acetyl val. 38-41; iod. val. 101-109; sol. pt. 7° C. **Fatty acids** have neut. val. 201 and iod. val. 111-112.

Grape-seed Oil.—Acid val. 16; sap. val. 178-179; Reichert-Meissl val. 0.46-2.0; iod. val. 94-97. **Fatty acids** have neut. val. 187 and iod. val. 98-100.

Castor Oil, obtained principally from the seeds of *Ricinus communis*, consists mainly of the glyceride of ricinoleic, isoricinoleic, and dihydroxystearic acid, together with a little tristearine. It is a very viscous oil, miscible with absolute alcohol and glacial acetic acid in every proportion and much used as a medicine and lubricant, but also for manufacturing Turkey red oils (which see).—Sp. gr. 0.960-0.966 (15° C.); sol. pt. −10° to −12° C.; sap. val. 176-183; iod. val. 83-86; refract. index, 1.480 (15° C.); viscosity 1160 secs. at 37° C.; Reichert-Meissl val. 1.1. Mixed fatty acids, M.P. 13° C.; Maumené, 47.

Blown Oils, Oxidised Oils, Soluble Castor Oils.—When semi-drying vegetable oils, blubber oils, and liquid waxes are placed in a vessel provided with a steam heating coil, and warmed from 70°-115° C., while a current of air is blown through, the oils oxidise to viscid, dense fluids which are miscible with mineral oils. They form valuable lubricating oils, approaching castor oil in mechanical properties; since castor oil is insoluble in mineral oils (and so cannot be mixed with them), such oils are known commercially as "**Soluble Castor Oils.**"

Turkey Red Oils, Sulphonated Oils are viscous, transparent liquids used in the preparation of cotton fibre for dyeing and printing Turkey red. Concentrated sulphuric acid is slowly run, with constant stirring, into castor oil, the temperature being kept below 35° C. during the whole course of the reaction. The product is washed with water, settled, the lower layer drawn off and washed with a solution of Glauber's salt until only slightly acid; finally ammonia or soda is added until the sample will give a complete emulsion with water. Turkey red oil F. is completely soluble in water. Turkey red oil S. is only partially soluble in water. See p. 549.

Nitrated Oils are heavy, viscid liquids obtained by treating castor (or linseed) oil with a mixture of 2 parts of concentrated sulphuric acid and 1 part of concentrated nitric acid (sp. gr. 1.5). They form homogeneous mixtures with nitro-cellulose. Thus a product resembling ebonite is obtained by mixing 1 part of nitrated castor oil with 9 parts of nitro-cellulose. Dissolved in acetone, these nitrated oils form varnishes which are capable of enamelling leather and mixing paints.

For **Bone Oil,** see p. 420.
For **Essential Oils,** see p. 132.
For **Rosin Oil,** see p. 339.
For **Oil of Turpentine,** see p. 337.

(*c*) Semi-drying Vegetable Oils.

These absorb oxygen from the air and become thick, without, however, completely drying up. Iodine value from 95-140.

Cotton-seed Oil is produced on an enormous scale in North America from the seeds of the various sorts of cotton trees; 17,000 tons, of value £580,000, were imported into Britain in 1910. It consists of glycerides of palmitic, oleic, and various unsaturated and hydroxy acids which cause the oil to somewhat rapidly oxidise at ordinary temperatures. It is, therefore, a weak drying oil. When cooled it deposits a large amount of cotton-seed stearin. Used as an edible oil, for adulterating lard, in the manufacture of margarine, soap, and lubricants.—Sp. gr. (15° C.) 0.922-0.930; sol. pt. 3°-4° C.; sap. val. 191-195; iod. val. 105; refract. index, 1.478 (15° C.); Maumené, 74°-78° C. Fatty acids have M.P. 35°-38°; neut. val. 201-208; iod. val. 110-115.

Test for Cotton-seed Oil.—Dissolve 5 c.c. of the fatty acids from the oil in 2 c.c. alcohol in a test tube. Heat to boiling on water bath; add 2 c.c. of $2N.AgNO_3$ solution; an immediate black colour shows presence of cotton-seed oil. Five per cent. of cotton-seed oil can be detected in rape or olive oil by this test.

Rape or Colza Oil, Sweet Oil, obtained from the seeds of *Brassica campestris*, contains considerable quantities of rapic acid, $C_{17}H_{32}.OH.COOH$, and other unsaturated oxy-acids. Being cheap, it is much used for lubricating and edible purposes. The pure oil on exposure to air remains fluid for some days, but long exposure causes it to thicken somewhat and become rancid. If adulterated with drying oils it rapidly turns into a jelly-like mass, or even becomes solid.—Sp. gr. 0.914-0.918; sap. val. 170-178; iod. val. 94-107; Hehner val. 95; Reichert-Meissl val. 1 c.c.; viscosity, 330-380 secs. at 21° C., 91-94 secs. at 60° C.; Maumené test, 60° C. The elaïdin test is here very useful for detecting presence of drying oils in rape oil. The fatty acids have sol. pt. 13°-18°; neut. val. 185; iod. val. 96-104.

Sesamé Oil, obtained from the seeds of the sesamé plant, *Sesamum indicum* and *orientale*, is a valuable edible oil consisting of a mixture of the glycerides of stearic, palmitic, oleic, and linolic acids. To detect the presence of the oil, dissolve 0.1 g. sugar in 10 c.c. HCl (sp. gr. 1.19); add 20 c.c. of oil; shake and allow to stand: crimson colour in the aqueous filtrate shows presence of sesamé oil.—Sp. gr. (15° C.), 0.914-0.916; sap. val. 188-195; sol. pt. −5° C.; iod. val. 103-112; Maumené, 65°-72° C.; Reichert-Meissl, 0.7 c.c.

Sunflower-seed Oil.—Acid val. 0.2-6; sap. val. 190-193; iod. val. 118-136; Maumené, 67°-75° C. Fatty acids have sap. val. 201 and iod. val. 124-134.

Maize Oil, Corn Oil.—Obtained from germs of the maize plant, *Zea Mays*, L. The germs are a by-product in glucose and starch works using maize as their raw material. Acid val. 2-20; sap. val. 187-190; Hehner val. 88-94; Reichert-Meissl val. 0.3-10; iod. val. 113-129. Fatty acids have neut. val. 200 and iod. val. 121-127.

Pumpkin-seed Oil has acid val. 3.5-19; sap. val. 188-195; iod. val. 104-130.

Black Mustard Oil has acid val. 5-8; sap. val. 173-175; iod. val. 98-110.

White Mustard Oil has acid val. 5-6; sap. val. 170-171; iod. val. 92-96.

Soja Bean Oil, from the seeds of *Dolichos Soja*, L., *Soja hispida*, *Soja japonica*, etc., plants indigenous to Manchuria, Japan, China. The seed contains 18 per cent. oil and 30-40 per cent. protein, and yields 13 per cent. oil. The expressed meal is made into bean-cakes; the Soja bean industry being one of the most important of Manchuria and Japan, 1,500,000 tons of oil being exported in 1911. The oil consists of glycerides of oleic and linolic acids, dries on standing to a thin skin, and is used for edible and illuminating purposes in the Far East; now used as a paint and linoleum oil. See Toch, *Jour. Soc. Chem. Ind.*, **31**, 572 (1912).—Sp. gr. 0.924; sap. val. 190-193; iod. val. 121-124; Maumené, 59°-61°; sol. pt. +8°-15° C. The fatty acids have a M.P. 27°-29°; sol. pt. 25°; iod. val. 115-122.

(*d*) Drying Vegetable Oils

These absorb oxygen from the air and dry up to a hard skin. They have an iodine value usually over 140.

Hempseed Oil has a sap. val. 190-195 and an iod. val. 140-166; Maumené, 95°-98°. Separated fatty acids have a sol. pt. 14°-16°; iod. val. 122-140.

Candle-nut Oil has a sap. val. 184-193 and an iod. val. 136-163.

Niger-seed Oil has a sap. val. 189-192 and an iod. val. 126-134.
More important than these are the following:—

Poppy-seed Oil, a pale yellowish oil obtained by pressing from seeds of the poppy, is used as a salad oil and for making artists' paints: a good drying oil.—Sp. gr. (15° C.) 0.92-0.97; sap. val. 192-197; iod. val. 137-143; Reichert-Meissl val. 0.0; Hehner val. 95; Maumené test, 88° C.; refract. index, 1.477 (15° C.). Fatty acids have sol. pt. 16.5; neut. val. 199; iod. val. 139; refract. index, 1.451 (15.5° C.). The differentiation of poppy oil from walnut oil—*e.g.*, in the examination of white paints—is achieved most readily by the hexabromide test (which see); walnut oil yields 1.4-2 per cent. of hexabrominated glycerides, poppy-seed oil none.

Walnut Oil, a very good but expensive drying oil obtained from the seeds of the common walnut tree; being almost colourless, it is used for making the best white paints for artists, such paints being less liable to crack than those made from linseed oil. For distinction from poppy-seed oil see the latter. It is frequently grossly adulterated with mineral oil.—Sp. gr. 0.925-7 (15° C.); sap. val. 192-198; iod. val. 143-151; Maumené test, 96°-110° C.; Reichert-Meissl val. 0.0; Hehner val. 95. Fatty acids solidify at 16° C., and have iod. val. 150.

Tung Oil, Chinese Wood Oil, Wood Oil, a very important drying oil possessing a characteristic odour and an even more pronounced drying power than linseed oil (giving, however, a *wax-like, non-elastic* product which renders it quite useless for paints in its ordinary condition), and when heated alone in absence of oxygen to 180°-250° C., it polymerises to a solid mass. It is said to be used for adulterating Chinese lacquers, and has been used in a solidified form for linoleum manufacture (see p. 50). In 1906 28,685 tons were exported from Hankow while the home consumption in China may amount to 60,000 tons. It is obtained from the seeds of *Aleurites cordata* and other trees growing in China, Japan, Tonkin, Annam, etc. It consists principally of glycerides of *oleic* and *elæomargaric acids*.—Sp. gr. 0.94; sap. val. 190-195; iod. val. 149-167; Maumené, 300°-372°. Separated fatty acids have sol. pt. 31°-37°; neut. val. 189; iod. val. 145-160.

LINSEED OIL AND PRODUCTS DERIVED THEREFROM

Linseed Oil, a yellowish brown fluid from the seeds of the flax plant, *Linum usitatissimum*, is largely used for paint, varnish, oil-cloth, linoleum, and soft soap manufacture. The oil is principally composed of glycerides of unsaturated acids like isolinolenic acid (58 per cent.), linolenic acid (13 per cent.), linolic acid (13 per cent.), oleic acid (4 per cent.). The oil rapidly absorbs atmospheric oxygen, with formation of a tough resinous mass and hence is a "drying oil." This drying property is increased by heating to 180° C. or by the addition of metallic salts—"driers"; 38,000 tons, value £1,250,000, were imported into England in 1910.

Constants of Linseed Oil.—Sp. gr. (15° C.) 0.93-0.94; sap. val. 190-195; iod. val. 173-193; Reichert-Meissl val. 0.00; Hehner val. 95; Maumené test, 103°-145° C.; refract. index (15° C.), 1.4835; viscosity (21° C.), 212 secs. Flash-point about 243° C. (470° F.). **Mixed fatty acids** solidify at 13°-17° C.; melt at 17°-24° C.; neut. val. 196-199 and iod. val. 179-200.

To test the drying properties of linseed oil, smear a glass plate with the sample and expose in the water oven. Note how long it takes to dry, also the nature of the residuum; compare with a standard sample treated in the same manner.

To find presence of driers incinerate 50 g. in a large porcelain crucible and analyse residue for metals.

To find whether suitable for linoleum-making heat some in a copper basin to 260° C., stirring and blowing air through the mass. Dense fumes are evolved and after a time it becomes thicker. A specimen is drawn out and cooled. It should be "stringy," *i.e.*, capable of being drawn out into threads. Compare with a standard sample of oil treated similarly. Adulteration with mineral oils lowers the saponification value.

The Chemistry of the Driers.*—The chemical changes taking place when linseed oil "dries" or "sets" are very complex, and, although they have been carefully studied by numerous different investigators, our knowledge of the same is very indefinite and unsatisfactory. We do know, however, that it is the result of oxidation, for the oil may be stored unchanged for an indefinite time in vacuo, or in the presence of an inert gas such as nitrogen. When oxygen can gain access to the oil, an increase in weight becomes apparent, and an elastic solid called "linoxyn" is produced, resulting in the "drying" of the oil. The term "drying," however, is misleading, for it implies that water has evaporated, leaving a solid residue—which is not the case.

We are not to suppose that linoxyn is a single substance, or that it is produced by the mere addition of oxygen to the linseed oil molecule. During the process of drying, not only is oxygen absorbed, but formaldehyde, and carbonic and formic acids are simultaneously liberated, showing that very complex reactions are taking place.

It has been known for many years that certain substances can accelerate the setting of linseed oil, and they are therefore known as "driers." The actual way in which these bodies act is obscure. Owing to the fact that some of the most common driers were highly oxygenated bodies, like manganese dioxide (MnO_2) and red lead (Pb_3O_4), a very plausible theory was advanced, according to which the driers themselves gave up to the oil the necessary oxygen to induce setting. When, however, quantitative experiments were performed, and proved that a ton of linseed oil can absorb from 3-5 cwt. of oxygen,† whereas only about 5 lbs. of drier are added to the same weight of oil, it was evident that such a theory was, to say the least, very incomplete. This led to the enunciation of the so-called "catalytic theory of driers," according to which the driers act as catalysers, that is to say, they assist the oil to take up oxygen without themselves undergoing a permanent alteration. The exact way in which this is done is uncertain, but it is usually assumed that when suspended in the oil or paint they unite with the atmospheric oxygen to form unstable, highly oxygenated bodies, which hand over their excess of oxygen to the oil almost immediately, being themselves reduced to their original condition. They are now in a position to unite with more oxygen, and to yield that up again in a precisely similar manner to the oil. And so the process goes on indefinitely until the oil has set.

The two main facts that may be cited in favour of this theory are as follows:—

1. A small quantity of drier is able to effect the rapid oxidation of a large amount of oil.

2. The best driers are the oxides or salts of those metals which are known to exist in various stages of oxidation, and to be readily oxidised to, or reduced from one state to another. Thus, for example, manganese, lead, and iron, from which the bulk of the best driers are prepared, each yield a series of well-defined oxides containing varying proportions of oxygen.

In the accompanying table‡ a list is given of the common driers, together with the percentage of metal usually found in them. The theoretical percentage of metal cannot always be given, as the composition of the finished product varies according to circumstances, the amount of water of crystallisation in particular being dependent upon the temperature at which the salts are prepared.

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* For a more detailed discussion of the action of driers on linseed oil the reader is referred to "An Introduction to the Chemistry of Paints," by J. Newton Friend (Longmans & Co., 1910).

† This is based on the fact that during the process of setting, linseed oil has been observed to absorb from 15-18 per cent. by weight of oxygen gas.

‡ This table is taken from Friend's "Introduction to the Chemistry of Paints," p. 155, the data having been calculated from the results given by T. A. Davidson in his paper entitled "The Action of Driers on Linseed Oil," read before the Paint and Varnish Society, 12th November 1908.

TABLE OF COMMON DRIERS.

Name.	Colour.	Per Cent. Metal in Pure Drier.	Per Cent. Metal in Commercial Drier.
Litharge	Buff	90.3	89.4
Red lead	Red	90.1	86.7-87.6
Lead acetate	White	54.6	52.4-53.3
,, linoleate	Brown	...	31.2
,, oleate	Yellow	...	22.6
,, rosinate (fused)	Yellow-brown	...	15.6
,, ,, (ppted.)	Light brown	...	...
Manganese borate	Pinkish	...	7.8-23.8
,, carbonate	Buff	...	38.8-42.6
,, dioxide	Black	63.2	50.4-54.3
,, hydroxide	Brown	...	46.5
,, linoleate	Dark brown	...	7.8-8.9
,, oleate	Brown	...	8.1
,, oxalate	Pinkish	...	30.2
,, rosinate (fused)	Dark brown	...	2.3-3.5
,, ,, (ppted.)	Pinkish	...	5.0-6.1
,, sulphate (anhydrous)	Pinkish	36.4	...

As is evident from the above table, a considerable variety of substances are placed under the category of driers. In the case of the metallic salts the efficiency is influenced to a slight extent by the nature of the acids with which the metal is combined. If this latter is favourable to the catalytic action, the drier is slightly more powerful than might otherwise be expected. This is true of rosinic acid, and metallic rosinates have of late found great favour amongst painters generally. They may be prepared by fusing together rosin and a metallic oxide, a product free from moisture being obtained, and known as a "fused" drier. "Precipitated" driers, as their name implies, are obtained by mixing solutions of alkaline rosinates with a soluble metallic salt, whereby the drier is precipitated. Such driers always contain a considerable quantity of moisture, up to, say, 6 per cent., and are thereby readily distinguished from fused driers. Other organic salts, such as the oleates and linoleates of lead and manganese, are also very efficient driers. Lewkowitsch has recently prepared tungates of these metals from the fatty acids of tung oil.

Since these organic compounds are readily soluble in turpentine and linseed oil, they are known as "soluble" driers. Solutions in either or both of these solvents are termed "liquid" driers or terebines.

It does not always follow, however, that the most powerful driers are necessarily the best for all work; other properties should be taken into consideration. For example, lead acetate is well known to be weaker than red lead and litharge, nevertheless it is used extensively in the manufacture of patent driers because it does not darken the oil so much—a point of considerable importance when white and light coloured pigments are being used. Ferrous sulphate should be used with care as it tends to render the film of oil brittle.

Now, according to the catalytic theory, chemically inert substances cannot be expected to function as driers. Nevertheless Hurst* found one "patent" drier to contain more than half its weight of calcium sulphate, whilst another contained 77 per cent. of barium sulphate (barytes) and silica. It would be unwise, with our present limited knowledge, to assume that chemically inert bodies are necessarily useless as driers, for it may well happen that the introduction of fine particles of solid into the oil can assist in some physical manner the absorption of oxygen, just as we know fine powders can greatly accelerate the oxidation of combustible gases. At present the only method of determining whether or not a drier is of any value is to test it experimentally in some such manner as that indicated below.

* See "Painters' Colours, Oils, and Varnishes," by Geo. Hurst (Griffin & Co., 1906), p. 437.

Turpentine is not infrequently regarded as a drier, but the researches of W. N. Hartley would seem to indicate that such is not the case in the strictest sense of the term. Turpentine assists in the drying of the oil by rendering it thinner, so that the painter can spread it over a larger surface, and thus come into contact with a proportionately greater quantity of air. It is not impossible, however, that whilst the above is the main function of the turpentine, a catalytic action does take place to a small extent in addition, for it is well known that turpentine readily absorbs oxygen from the air, yielding, as many chemists believe, an organic peroxide, which latter would act on the oil in an analogous manner to an inorganic peroxide.

In the case of litharge and red lead, complications arise owing to tendency which these oxides exhibit to saponify the oil, whereby an insoluble lead soap is produced, which produces a more brilliant coat on drying than the pure oil alone. To what extent this saponification assists the rate of drying is at present unknown.

Practical Testing of Driers.*—The old method of testing driers by noting the time taken by a thin film of terebine to set hard on glass cannot be too strongly condemned, for it leads to most conflicting results. One of the most satisfactory methods is that given by T. A. Davidson.† This investigator prepares a series of mixtures of linseed oil and drier in varying proportions. These are kept at a uniform temperature for a number of hours in separate stoppered bottles. The liquids are now filtered through paper into fresh bottles, and a portion of each is run on to a glass slide and placed in an air oven at constant temperature. From time to time the slides are examined and the number of minutes or hours noted that are required before the film is sufficiently firm to bear the finger being gently drawn across it without leaving a whitish mark. This time is known as the "setting value," is greatly affected by a number of factors, such as temperature, rate of change of air, thickness of the oil film, moisture, and the nature of the surface to which the oil is applied. In testing a drier, therefore, it is necessary to perform two series of experiments at the same time and under precisely similar conditions, one with a standard drier, whose efficiency is well known from practical experience; the other with the sample to be tested. Only in this way is it possible to arrive at satisfactory and reliable results.

Varnishes, Lacquers, and Enamels

Varnishes, lacquers, and enamels, when applied to the surfaces of bodies, have in general two functions to fulfil, namely, those of protection and of ornamentation.

Oil Varnishes were first manufactured on a commercial scale in England at the close of the eighteenth century, and are prepared by dissolving resins in linseed oil. Owing to the fact that the resins are, as a rule, insoluble in the oil before fusion, varnishes cannot be prepared by simply mixing the ingredients at the temperature of the room. The resins are first fused in copper gum pots, and a quantity of oil already at 500° F. (260° C.) is added under vigorous stirring. The contents of the pot are now run into a large iron tank capable of holding the "runnings" of several pots, and the temperature maintained at 500° F. until the varnish has cleared and is stringy. It is then cooled, thinned with turpentine, and stored to clear and age.

Simple as the above process appears to be in theory, years of practice are required to produce thoroughly satisfactory results. If the resin is not properly fused it cannot undergo thorough union with the oil, the imperfectly fused portions remaining suspended as very fine insoluble particles in the varnish, instead of being dissolved in the same. The result is that when the varnish is applied to any surface it sets with a "bloom." Whilst this is not the only cause of blooming it is a sufficiently common one to merit attention.

For pale varnishes it is essential that the resins employed be pale, and, unless the temperature of the gum pot is carefully watched and maintained as low as possible, the resins will darken and spoil.

These technical difficulties, coupled with the fact that the already costly resins lose from 5-20 per cent. in weight during fusion, has led to many attempts on the part of manufacturers to employ some other method. Experiments have been

* This subject is dealt with in further detail in Friend's "Introduction," etc., p. 161 *et seq.*
† Davidson, *loc. cit.*

carried out with terpineol, with amyl alcohol, and with naphthalene and phenols as solvents, but with doubtful success.

Enamels consist of oil varnishes into which certain finely levigated pigments, such as zinc oxide and venetian red, have been thoroughly ground. Black enamels are usually prepared from asphaltum.

Spirit Varnishes are prepared by mixing resins with such solvents as methylated spirit or turpentine, and allowing to stand in a warm place. Excessive heat must be avoided, owing to the volatile nature of the solvents, and the inflammability of their vapours. The methylated spirit employed should not be weaker than 64 over proof.

Nitro-cellulose Varnishes.—Varnishes used in the manufacture of artificial leather and in special lacquer work consist of nitro-celluloses dissolved in amyl acetate and suitably coloured. About 450,000 gallons of amyl acetate are annually employed in the United States for making such nitro-cellulose varnishes. These varnishes are likewise used for painting iron work owing to their non-porous nature.

Water Varnishes are made by dissolving gums or glue in water. If, just before use, a small quantity of potassium bichromate is added to glue varnish, the coat is rendered almost waterproof.

Natural Varnishes.—Two genera of plants belonging to the *Anacardiaceæ* yield a sap on tapping, which is used in the Far East as a natural varnish or lacquer, namely, *Rhus* for Japanese and Chinese lacquers, and *Melanorrhea*, which yields black Burmese varnish. Japanese lacquer is hard, its hardness increasing with age. Its great value lies in its persistent lustre, and to the resistance which it offers to such agencies as spoil our ordinary oil varnishes. It should be borne in mind that the so-called lac ware of India is not true lacquer ware, as it is produced by the aid of shellac dissolved in suitable liquid menstrua. The chief Chinese tree yielding lacquer is *Rhus vernicifera*, native to that country, and, like the art of lacquering, introduced from China into Japan. Chinese lacquer is frequently adulterated with tung oil. When first obtained from the tree it is greyish white in hue, but quickly oxidises and becomes brownish black. The Japanese lacquer is very similar. Both lacquers harden only in a moist atmosphere, hence in China lacquering is performed in wet weather, and in Japan it is conducted in special moisture-laden rooms. Oxygen is slowly absorbed during the setting to the extent of 5.75 per cent. of the weight of the original varnish. The only methods of thinning the lacquer known to the Japanese are by warming, or by addition of camphor. For this reason camphor wood is not used as the foundation for lacquer, although almost any other kind of wood may be employed.

Solidified Linseed Oil, Linoxyn, Oil Cloth and Linoleum

LITERATURE

See REID, *Journ. Chem. Soc. Ind.*, 1896, 75.
INGLE, *loc. cit.*, 1904, 1197.
A. DE WAELE and O. J. PATRICK, "Linoleum": Its Manufacture and Valuation, *loc. cit.*, 1915.

The technical literature is poor, and much of the materials for the accompanying article were privately communicated by firms interested in the trade.

Linseed oil rapidly takes up oxygen and solidifies to a flexible solid mass of unknown constitution, termed "solidified linseed oil," "oxidised linseed oil,"

"linoxyn," etc. The substance is manufactured on a large scale by several different processes (F. Walton, 1860-63).

1. Linseed oil, freed from moisture by settling (sometimes by filtering through dry salt)—otherwise frothing ensues on boiling—and boiled with a drier to accelerate oxygen absorption, is allowed to flow down a light cotton fabric ("scrim") suspended from the ceiling of a high room which is maintained at 38° C. The flooding with oil takes place daily, and each layer solidifies in about twenty-four hours. The process is continued for six to eight weeks, the oil dripping from the cloth being drawn off and allowed to flow again down the cloth. When the layer of solidified linseed oil is half an inch thick, the "skins" (25 ft. long) are cut down, and the mass passed between rollers. It is known as "scrim oil." The scrim at first supports the oil, but before the skins are ready to be cut down the cotton is so thoroughly rotted that it readily disintegrates, and cannot be traced in the subsequent processes through which the oil passes.

2. Raw linseed oil is placed in a horizontal steam-jacketed cylinder within which a central shaft provided with arms rotates with high velocity. The cylinder is only half filled with oil, and the arms beat it up into a fine spray, while at the same time a current of air is driven through. Steam in the jacket is maintained so as to heat the oil to a proper temperature (which differs with the kind of oil to be produced). As the oxidation proceeds the temperature rises, and the steam is now replaced by cold water. The oil is oxidised in five to six hours, but if an oil of a light colour is required, twenty-four hours is required. The thick viscous liquid is run while hot into trays where it solidifies on cooling. At this stage it is not so thoroughly oxidised as scrim oil, and (except when used for cork carpet) the trays have to be kept in stoves at a temperature of about 38° C. for from four to eight days until the desired degree of oxidation is obtained.

In this forced method of oxidation there is a loss of about 8 per cent., whereas, in the natural oxidation of the scrim method there is an actual gain of about 7 per cent. The oil oxidised in this manner is more liable to spontaneously ignite than that produced by the scrim process. The oil is not quite so elastic as that prepared by the "scrim" process, owing to part of the oxidised oil being "superoxidised" to a liquid substance, first discovered by Reid.

3. A third process for reducing linseed oil to a thick mass suitable for mixing with ground cork, etc., for linoleum making is achieved by prolonged boiling alone, which causes the oil to polymerise. A considerable proportion of the linoleum sold at the present day is made from oil so prepared. The manufacture of linoleum from polymerised linseed and tung oil has been patented by Dewar and the Linoleum Manufacturing Company (English Patent, 5,789, 1903). See p. 45.

Linoleum and Oil-cloth Manufacture*

The first step in the manufacture of linoleum is the production of "linoleum cement." This is done by melting the solidified oil with various gum resins (usually kauri gum and rosin), and mixing with it cork flour and various pigments and fillers. The linoleum composition thus obtained is finally rolled on to canvas. A good elastic cement is composed of about 8½ cwt. of oxidised oil, 1 cwt. rosin, and 3 cwt. kauri gum; sometimes copal is added. Each manufacturer, however, uses his own formula, and this is carefully kept as a trade secret. The kauri is pulverised, but the rosin can be used in lumps since it acts as a flux. The mixing operation is carried out in a steam-jacketed vessel provided with stirrers. Samples are withdrawn from time to time and tested. It is of the greatest importance that no overheating takes place. When thoroughly mixed, the "cement" is run into pans, and in summer is sometimes artificially cooled, since large masses of this (as well as the oxidised oil) have been known to heat and spontaneously inflame. The cement is cut into small pieces, mixed with rather more than its weight of ground cork, passed through steam-heated mixing rolls, more thoroughly amalgamated in a

* See Reid, *Journ. Soc. Chem. Ind.*, 1896, 75; Ingle, *loc. cit.*, 1904, 1197.

mixing drum (various colouring matters being here added according to the colour desired for the finished linoleum) and then passed into a "German"—an apparatus resembling a large sausage machine, but very strongly made. At first steam heating is necessary, but once the machine is working the heat generated by friction keeps the mass soft, and in summer it is even necessary to circulate cold water in the jacket instead of steam. From the "German" the linoleum issues as lumps or pellets, and is passed through mixing rolls, in which it is converted into sheets, and finally is rolled upon jute canvas by means of steam-heated rolls. The canvas back is protected by a varnish ("backing") spread upon it by means of a special machine; the main ingredients of the backing are oxidised oil and varnish, or varnish bottoms mixed with ochres or oxides; the material is fluid when hot, but solidifies on cooling. Finally the linoleum is "seasoned" in rooms at 23.5° C., best in horizontal racks.

Linoleums may be grouped into (1) Plain and Printed; (2) Inlaid; (3) Cork Carpets.

The **Plain Linoleums** consist essentially of cork, pigment, and cement rolled on canvas; they are printed with oil colours so as to produce designs ("**printed linoleums**"). The oil paints, however, in time wear off, and efforts were made to produce coloured patterns running right through the thickness of the coating composition, thus introducing "**inlaid linoleums**." This requires special machines of extreme ingenuity. Differently coloured linoleum compositions are granulated and moulded into the required shapes, and placed upon the canvas in such a way as to produce the required design; an alternative method is to roll the differently coloured compositions into sheets, and cut from these sheets various forms and stamp them upon the canvas. The patterns thus built up are immediately welded together by heat and pressure, and afterwards seasoned. Details of these special processes will be found in the patent literature. All inlaids contain a large proportion of wood flour in addition to cork dust.

Granite Linoleums are of this class. The "granite" effect is produced by mixing together granules of differently coloured linoleum compositions before pressing the material on to the canvas. In these inlaid linoleums the proportion of cement is generally rather more than that of cork and wood flour, so as to ensure a thorough welding of the various linoleum compositions forming the design.

In **Cork Carpets** the cork grains are larger, and wood dust is never employed, while the quantity of pigment is usually smaller than in the plain and inlaid varieties. Both kinds of cement are used.

Oil-cloth consists simply of fabrics coated with linseed oil, whiting, and pigment, and are printed in oil colours in the usual way.

The colours used in linoleum and oil-cloth manufacture are—

Red.—Red oxides, or, in the case of bright inlaid colours, permanent lakes.
Blue.—"Ultra" blue.
Green.—Chrome green and Brunswick green.
White.—White lead, lithophone.
Yellow.—Chromes.
Black.—Vegetable black.

The authors' best thanks are due to Mr A. H. Dewar, F.I.C., manufacturing manager of the Linoleum Manufacturing Co. Ltd., who gave us much information regarding the modern methods used in manufacturing linoleum.

Statistics.—The amount of **oil-cloth** and **linoleum** imported into the United Kingdom in 1910 was 1,060,000 sq. yds., of value £71,700. The amount exported is shown by the following figures:—

		Quantities.		Value in 1910.
		1906.	1910.	
Oil-cloth—				£
For floor coverings	Sq. yds.	37,395,100	36,123,800	1,932,742
For furniture coverings	,,	8,206,200	15,773,700	611,602
For all other purposes	,,	3,272,700	2,394,800	87,297
Total of oil-cloth	,,	48,874,000	54,292,300	2,631,641

The **United States** in 1910 imported 4,800,000 sq. yds. (value, $1,834,000) of oil-cloth and linoleum; the export of floor oil-cloth reached $128,000 in 1910, the value of other kinds of oil-cloth exported being returned as $353,000.

ANIMAL AND VEGETABLE WAXES (NON-GLYCERIDES)

LITERATURE

See under Oils, Fats, and Waxes. Special works dealing with waxes alone are—

L. SEDNA.—"Das Wachs und seine technische Verwendung." Vienna, 1902.

T. W. COWAN.—"Wax Craft: All about Beeswax." London, 1908.

The manufacture of ordinary commercial "sealing wax" (which usually does not contain true wax) is dealt with in the following works:—

H. C. STANDAGE.—"Sealing Waxes." London, 1902.

L. E. ANDÉS.—"Siegel- u. Flaschenlacke." (Vienna, 1885).

W. ELLRAM.—"Siegel- und Flaschenlackfabrikation." Lodz, 1900.

The waxes are esters formed by the union of fatty acids and alcohols not belonging to the glycerol series. Hence waxes are sharply distinguished from fats in that they contain no glycerol; they have, however, many properties in common with true glycerides (fats); thus they can be saponified with alkalies, the salts of fatty acids and alcohols being obtained:—

$$\underset{\text{The wax "myricin."}}{C_{15}H_{31}CO.O.C_{30}H_{61}} + KOH = \underset{\text{Pot. palmitate.}}{C_{15}H_{31}COOK} + \underset{\text{Myricyl alcohol.}}{C_{30}H_{61}OH}$$

The saponification is much more difficult to carry out in the case of waxes than in the case of fats. Wool wax, for instance, must be boiled with alcoholic potash for at least twenty hours; moreover the higher alcohols, being insoluble in water, occur in the "unsaponifiable" residue. This allows us to readily distinguish fats from waxes; for whereas most fats yield 95 per cent. of fatty acids, the liquid waxes yield only 60-66 per cent., the remaining 40-34 per cent. being made up of monovalent alcohols, among which we may mention:—

Ethane series. $C_nH_{2n+1}.OH$.

Cetyl alcohol	$C_{16}H_{33}.OH$.
Octodecyl alcohol	$C_{18}H_{37}.OH$.
Carnaübyl ,,	$C_{24}H_{49}.OH$.
Ceryl ,,	$C_{26}H_{53}.OH$.
Myricyl ,,	$C_{30}H_{61}.OH$.
Psyllostearyl ,,	$C_{33}H_{67}.OH$.

Aromatic alcohols.

Lanolin alcohol	$C_{12}H_{23}OH$.
Cholesterol	$C_{27}H_{45}OH$.
Isocholesterol	$C_{27}H_{45}OH$.
Phytosterol	$C_{27}H_{45}OH$.
Sitosterol	$C_{27}H_{45}OH \times H_2O$.

Liquid Waxes

Sperm Oil, from the blubber and head cavities of the sperm whale, consists of combinations of unknown alcohols with fatty acids. Cooled to low temperatures the oil deposits **spermaceti** (which see). The oil is a valuable lubricant, especially for rapidly running machines; since it does not become gummy or rancid it can be used for delicate machinery such as watches. It retains its viscosity at high

temperatures. Sperm oil is used for lubricating, illuminating, dressing leather, and tempering steel.—Sp. gr. (15° C.), 0.880-0.883; sap. val. 123-133; iod. val. 81-84; Reichert-Meissl val. 0.60; fatty acids, 60-64 per cent.; alcohols, 37-41 per cent.; Maumené test, 45°-51° C. If adulteration with fatty acids has taken place glycerol will be found present. The percentage of glycerol multiplied by 10 will give the percentage of fatty oil.

Doegling or Bottlenose Oil is a fluid very similar to sperm oil, with almost identical constants; it can be distinguished from sperm oil by its taste. It has a lower price than the former oil on account of a slight tendency to "gum."

Solid Animal Waxes

Spermaceti, the white crystalline wax which separates from chilled sperm oil, consists principally of cetin (cetyl palmitate), $C_{16}H_{33}O.CO.C_{15}H_{31}$. The substance is a good candle material.—Sp. gr. 0.90-0.96 (15° C.), 0.80-1.81 (100° C.); sol. pt. and M.P. 44° C.; sap. val. 125-134; iod. val. 3.8; alcohols, 51.4 per cent.; fatty acids, 53 per cent.

Beeswax* is obtained from the honeycomb of bees by melting, straining from impurities, and running into moulds. Sometimes the wax is expressed. It may be bleached by exposure to sunlight, or by an oxidising agent such as nitric acid, chromic acid, or hydrogen peroxide. The ordinary yellow wax smells of honey, the bleached is white, inodorous, and tasteless, consisting mainly of myricyl palmitate, $C_{30}H_{61}O.C_{16}H_{31}O$, and cerotic acid, $C_{26}H_{52}O_2$.—Sp. gr. 0.962-0.975 at 15° C., 0.81-0.83 at 100° C.; sol. pt. 60°; M.P. 63° C.; acid val. 20; sap. val. 90; iod. val. 8-11; refract. index, 43°-45° (butyro-refractometer); fatty acids, 47 per cent.; unsaponifiable matter, 55 per cent.; Reichert-Meissl val. 0.3-0.5.

Insect Wax, Chinese Wax is obtained from an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood, which deposits the wax on certain trees. A hard, yellowish-white solid consisting mainly of ceryl cerotate, $C_{26}H_{51}O.CO.C_{25}H_{51}$. This body is used as a furniture and leather polish, for sizing paper and cotton goods, and as a candle material.—Sp. gr. 0.92-97 at 15°, 0.81 at 100° C.; M.P. 81°-83° C.; sap. val. 80-93; iod. val. 1.4; fatty acids, 51 per cent.; alcohols, 49 per cent.

Wool Wax, Wool Grease is the natural grease encrusting sheep's wool fibre. Before spinning, this grease is removed, sometimes by extracting with volatile solvents, but more usually by washing with soap and sodium carbonate solutions, with which the oil forms an emulsion; on adding sulphuric acid to this the grease separates. Since the process of wool washing gives rise to very large volumes of waste liquors containing much free and combined fat, complications ensue when these liquors are run off into sewers. In the case of Bradford £12,000 per annum is expended for sulphuric acid with which to separate the fatty matter from the sewage.† The recovered fatty acids are sold under the name **Yorkshire grease** or **Wakefield grease** at £6 per ton, and 40 tons per week are recovered from the sewage. In large wool-washing works the suds are treated before running to waste, the grease being converted into lanolin, soap, and lubricating oil. In a works of moderate size 50 tons of grease are obtained monthly, and sold at £9 to £10 per ton.

The crude grease thus obtained is purified by various patented processes, and brought into the market under the name "**lanolin.**" Owing to the ease with which wool wax is absorbed by the skin it forms the basis of many valuable ointments and cosmetics. The chemical composition of wool wax is not exactly known; besides glycerides it contains stearic and palmitic ethers of cholesterol and isocholesterol,

* A complete account of beeswax, its manufacture and properties, is given by T. W. Cowan, "Wax Craft: All about Beeswax." London, 1908. See also W. F. Reid, *Journ. Soc. Arts* (1903), 522.

† *Jour. Chem. Ind.* (1909), 38, 14.

Summary.—The following tables, taken from A. C. Wright's "Analysis of Oils," summarise the chief chemical and physical properties of the better known oils :—

THE CHEMICAL PROPERTIES OF

	Acid Value.*	Saponification Value.	Hehner Value.
Drying oils—			
Linseed oil	1·8	187-196	94.8
Hempseed oil	1	190-195	...
Wood oil	0.7-10.7	(155-) 192-197	96.0-96.6
Candle-nut oil	...	184-192.6	95.5
Walnut oil	10	192-197	95.4
Poppy-seed oil	4·11	189-198	95.0
Niger-seed oil	5·12	189-192	94.1
Semi-drying oils—			
Sunflower-seed oil	0.2-6	190-193	...
Maize oil	2.2-20	187-190	88.2-93.6
Pumpkin-seed oil	3.5-19	188-195	96.2
Sesamé oil	0.2-8	188-192	95.6-95.8
Cotton-seed oil	0.4-2.2	190.4-197	94.2
Rapeseed oil	1.4-4.0	(169.4-) 173-178 (-181)	94.5-96.3
Black mustard oil	5·7-7·4	173-175	96.0
White mustard oil	5.4	170-171	95.8
Non-drying oils and solid fats—			
Earthnut oil	0.3-33	185.6-196	95.6
Almond oil	10	188-195	96.6
Croton oil	...	210.3-215.6	...
Grapeseed oil	16	178-179	...
Castor oil	0.4-0.8	173-183	...
Olive-kernel oil	2.0-3.5	182.3-188	...
Olive oil	0.6-5.0 (-25)	185-195	0.6
Ben oil	...	...	...
Neat's foot oil	0-0.7	194-197.4	95.3-95.5
Lard	...	195.3-196.6	95.8-96.15
Lard oil	0.4	193	97.4
Mahwa butter (*Bassia latifolia*)	4.8-70.8	187-194	94.7, 95.0
Mowrah-seed oil (*Bassia longifolia*)	...	188.4	...
Palm oil	...	196-202	...
Bone fat	...	172-194	86-94
Tallow (beef)	...	193-198	95.6
Tallow (mutton)	...	195	95.5
Tallow oil	...	197	...
Cocoa (cacao) butter	1.1-4.5	191.8-194.5 (-200)	...
Vegetable tallow	...	198.5-203.6	...
Butter fat	0.2-0.6	221-235	86.0-88.8
Palm-kernel oil	...	246-250	...
Japan wax	11-32	(206-212-) 217-222 (-237.5)	90.6
Myrtle wax	3	205.7-211.5	...
Cocoa-nut oil	10.0-35.2	255-263	82.3
Marine animal oils—			
Menhaden oil	0.2	189-192	...
Sardine oil	2.2-21.7	189.8-193.8	94.5-97.1
Cod-liver oil	0.3-31.9	(171-) 175-188	96.5
Seal oil	0.8-43.1	(178-) 189-193	95.4-96.0
Whale oil	0.3-51.4	184-200 (-224)	...
Porpoise oil	0.8	203.4-218.8	...
Dolphin oil	...	197-290	66.3-93
Liquid wazes—			
Sperm oil	0.4	(117-) 125-133 (-147)	...
Arctic sperm (bottlenose) oil	...	123-133	...
Solid waxes—			
Spermaceti	0.1-5	(108) 122.7-136	...
Beeswax	17.5-21	87.5-99	...
Carnauba wax	4-8	79-95	...
Wool wax	0.6-1.8	83-102.4	...

NOTES (see also the notes appended to the Table of Physical Properties, p. 59).

* The acid values frequently vary greatly; in most cases the higher value given is not to be regarded as a superior limit.

† The *total* volatile (soluble) acids may be calculated from the difference between the apparent and true acetyl values determined by Lewkowitsch's method, given in the next column. This difference, multiplied by $\frac{5}{5.6}$, gives (very nearly) the number of c.c. of decinormal potash required to neutralise the volatile acids contained in 1 g. of the fat.

Reichert-Meissl Value.†	Acetyl Value (Lewkowitsch's Method).		Iodine Value.‡	Insoluble Fatty Acids.	
	Apparent.	True.		Saponification Value.	Iodine Value.‡
0 (?)	12.5	11.7	(160-) 170-202	182-199	170-180 (?)
...	...	...	(140-) 155-166	...	141 (?)
...	...	...	150-170	(168)-189	(144-) 150-160
...	...	9.8	(136-140) 163.7	...	142.7-144
0	...	...	143-148	...	...
0	...	...	(120-) 128-137	...	139
0.1-0.6	...	...	126.6-134	...	...
...	...	...	118-132 (-136)	201.5	124-134
4.2-9.9	...	...	(113-) 118-128.6	200.0	121-126.4
...	...	...	113-130.7	...	...
0.35	...	...	104.8-110.4	195-199	109-112
...	7.7	7.6	(97.5-) 102.5-110	201-208	102.4-115
0.0-0.8	...	...	(94-) 98-105 (-110)	174-182	98-105
0	...	...	98.8-106 (-110.5)	...	110
0	...	...	92-96.7	...	96
0	...	...	(82-) 92-105	198	96-103.4
0	...	...	93-102	...	...
12-14	38.6-40.8	...	101-104.7	201	111.2-111.8
0.46	...	...	94-96.2	187	98-99
...	...	146.9	82.6-87	182-193	86.6-94
...	...	...	81.8-87.8	...	...
...	...	...	78-85 (-88)	196-200	86-90
...	...	...	80-84	...	...
...	...	...	67-72.9	200.6-201.2	(63.6-69.5) 74.5-75.8
...	...	...	55-63 (-68.8)	...	59.0-63.5
0	...	...	73-77.3	...	...
0.4-0.9 (1.23)	...	...	(29.9?) 53.4-67.8	206.0	(131.6?)
...	...	...	50.1	...	...
0.5	...	...	50-53.5	205-213	53
...	...	...	46-56 (-62)	201-206	55-57
0.5	6.6	4.6	average, 41-46	196-207	41
...	...	...		...	37.8
...	...	...	71.0-75.7	...	54.6-57
0.2-0.8 (-1.6)	2.8	2.0	32-37.0 (-41)	198	39.1
...	...	...	28-38	202-209.5	30.3-39.5
(11.2-) 24-33 (-41)	...	...	29-37	212.5-217	28-31
5	...	...	10-17	258-265	(3.6-) 12-13.6
(4.7-6 per cent. of soluble acids)	...	...	8.3-12.8	211-216	10.6
...	...	...	10.7	230	...
6.6-8.5	...	...	8.2-9.6	...	8.4-9.3
2.4	...	...	(148-) 175.6-183.1	...	...
...	...	...	134.1-191.7	...	...
0.2	4.75	1.15	(123-) 138.8-177	204	165-170
...	...	...	(91-94-) 125-146	...	...
Reichert value, 3.7-12.5	...	...	(81-) 106-131	...	130-132
22-24	...	...	126.9	...	...
Reichert value, 5.6-66	...	...	33-99	...	...
Reichert value, 1.3	7.1	5.4	78.7-84	...	...
...	6.7	5.4	80.4-82.1	...	...
...	4.6	2.6	4	...	...
...	17.4	15.2	8.8-10.7	...	...
...	57.5	55.2	13.5	...	...
...	32.6	23.3	(10-) 20-21 (-28)	...	...

‡ Iodine value. Low results were obtained in the older determinations owing to the use of an insufficient excess of the reagent. Low results in the case of the drying oils may also be due to the sample having undergone oxidation. Thus the lower figures given in the table represent values which may not now be expected.

	Specific Gravity.	Melting Point.	Solidifying Point.	Refractive Index.	The Insoluble Fatty Acids.		
					Specific Gravity.	Melting Point.	Solidifying Point.
Drying oils—		° C.	° C.			° C.	° C.
Linseed	$\frac{15.5}{15.5}$ 0.930-0.937 $\frac{99}{15}$ 0.8809	− 16 to − 20	16, − 27	15° C., 1.481 60° C., 1.4674	$\frac{15.5}{15.5}$ 0.923, $\frac{100}{100}$ 0.8925	17-24	13-17
Hemp-seed oil	$\frac{15}{15}$ 0.925-0.933	...	− 27.5	...	...	17-19	16
Wood oil	$\frac{15.5}{15.5}$ 0.934-0.943	...	Below − 17(?)	...	...	30-49	17-34
Candle-nut oil	$\frac{15.5}{15.5}$ 0.9256	...	...	15° C., 1.4756-1.4759	...	20-21	13
Walnut oil	$\frac{15.5}{15.5}$ 0.921-0.926	...	...	40° C., 1.4689-1.4710	...	16-20	14.3
Poppy-seed oil	$\frac{15.5}{15.5}$ 0.923-0.9268 (0.937)	...	− 18	40° C., 1.4680	...	20-21	16-19
Niger-seed oil	$\frac{15.5}{15.5}$ 0.9248-0.9270	...	Below − 9	40° C., 1.4678	...	...	...
Semi-drying oils—							
Sunflower-seed oil	$\frac{15}{15}$ 0.924-0.926	...	...	...	...	22-24	17-19.8
Maize oil	$\frac{15.5}{15.5}$ 0.924-0.928	...	− 36	15° C., 1.4765-1.4767 60° C., 1.4605	100° C., 0.8529	17-22.4	...
Pumpkin-seed oil	$\frac{15}{15}$ 0.917-0.925	...	− 15	25° C., 1.4723-1.4738	...	26.5-28.5	...
Sesamé oil	$\frac{15}{15}$ 0.921-0.926	...	...	15° C., 1.4746 60° C., 1.4580	...	24.2-31	18-28
Cotton-seed oil	$\frac{15.5}{15.5}$ 0.920-0.928 $\left(\frac{15}{15}\right.$ 0.930$\left.\right)$	...	...	15° C., 1.475 60° C., 1.4586	$\frac{100}{100}$ 0.8816	35-40	32-38
Rape-seed oil	$\frac{15.5}{15.5}$ 0.912-0.917	...	− 1 to − 10	15° C., 1.4745 60° C., 1.4584	$\frac{100}{100}$ 0.8758	17-21	12-16.5
Black mustard oil	$\frac{15.5}{15.5}$ 0.915-0.919	...	− 17.5	40° C., 1.4655	...	16-17	15
White mustard oil	$\frac{15.5}{15.5}$ 0.912-0.915	...	− 8 to − 16	40° C., 1.4649	...	15-16	...

Non-drying oils and solid fats—						
Earth-nut oil	$\frac{15.5}{15.5}$ 0.916-0.9256	...	−3 to −7	15° C., 1.4731 60° C., 1.4564	$\frac{100}{100}$ 0.8475-0.864	27-32	22-30
Almond oil	$\frac{15.5}{15.5}$ 0.917-0.9195	...	−10 to −21	25° C., 1.468-1.467 60° C., 1.4555	...	14	5-14
Croton oil	15° C., 0.940-0.960; 100° C., 0.8874	...	−16	27° C., 1.4768	...	...	16.4-19
Grape-seed oil	15° C., 0.920-0.596	..	−10 to −17	...	...	23-25	18-20
Castor oil	$\frac{15.5}{15.5}$ 0.960-0.967	...	−10 to −18	15° C., 1.4803 60° C., 1.4647	...	13	3
Olive-kernel oil	$\frac{15}{15}$ 0.918-0.920	...	...	1.4682-1.4688	...	...	...
Olive oil	$\left(\frac{15}{15}\right)$ 0.914) $\frac{15.5}{15.5}$ 0.917-0.920 $\frac{100}{100}$ 0.862-0.864	...	...	15° C., 1.4718 60° C., 1.4546	$\frac{60}{15}$ 0.878 $\frac{100}{100}$ 0.8749	22-26	21-24
Ben oil	$\frac{15}{15}$ 0.9120	...	...	...	...	...	...
Neat's foot oil	$\frac{15}{15}$ 0.914-0.919	...	...	15° C., 1.473 60° C., 1.4559	$\frac{100}{100}$ 0.8742-0.8800	28-30	16-26.5
Lard	$\frac{15}{15}$ 0.931-0.938 $\frac{60}{15.5}$ 0.886 $\frac{100}{15}$ 0.860-0.862	40-45	27-30	40° C., 1.458-1.460 60° C., 1.452	...	35-45	37-39
Lard oil	$\frac{15.5}{15.5}$ 0.917 100°, 0.8626	...	...	...	0.885	35	31
Mahwa butter (*Bassia latifolia*)	$\frac{100}{100}$ 0.8943-0.8975	23.0-31.0	19-22	40° C., 1.4605-1.4609	...	45	40
Mowrah seed oil (*Bassia longifolia*)	100° C., 0.8854	35.5-42	25-36	...	...	54 5-55.5	52.5
Palm oil	$\frac{60}{15.5}$ 0.8837 $\frac{100}{100}$ 0.858	...	...	60° C., 1.451	$\frac{100}{100}$ 0.870	47-50	40-45
Bone fat	$\frac{15.5}{15.5}$ 0.914-0.916 $\frac{60}{15.5}$ 0.894	21-22	...	60° C., 1.451	...	30-42	28-32

	Specific Gravity.	Melting Point.	Solidifying Point.	Refractive Index.	The Insoluble Fatty Acids.		
					Specific Gravity.	Melting Point.	Solidifying Point.
Drying oils—		° C.	° C.			° C.	° C.
Linseed	$\frac{15.5}{15.5}$ 0.930-0.937; $\frac{99}{15}$ 0.8809	− 16 to − 20	− 16, − 27	15° C., 1.481; 60° C., 1.4674	$\frac{15.5}{15.5}$ 0.923, $\frac{100}{100}$ 0.8925	17-24	13-17
Hemp-seed oil	$\frac{15}{15}$ 0.925-0.933	...	− 27.5	...	...	17-19	16
Wood oil	$\frac{15.5}{15.5}$ 0.934-0.943	...	Below − 17(?)	...	...	30-49	17-34
Candle-nut oil	$\frac{15.5}{15.5}$ 0.9256	...	...	15° C., 1.4756-1.4759	...	20-21	13
Walnut oil	$\frac{15.5}{15.5}$ 0.921-0.926	...	...	40° C., 1.4689-1.4710	...	16-20	14.3
Poppy-seed oil	$\frac{15.5}{15.5}$ 0.923-0.9268 (0.937)	...	− 18	40° C., 1.4680	...	20-21	16-19
Niger-seed oil	$\frac{15.5}{15.5}$ 0.9248-0.9270	...	Below − 9	40° C., 1.4678	...	...	...
Semi-drying oils—							
Sunflower-seed oil	$\frac{15}{15}$ 0.924-0.926	...	...	...	...	22-24	17-19.8
Maize oil	$\frac{15.5}{15.5}$ 0.924-0.928	...	− 36	15° C., 1.4765-1.4767; 60° C., 1.4605	100° C., 0.8529	17-22.4	...
Pumpkin-seed oil	$\frac{15}{15}$ 0.917-0.925	...	− 15	25° C., 1.4723-1.4738	...	26.5-28.5	...
Sesamé oil	$\frac{15}{15}$ 0.921-0.926	...	...	15° C., 1.4746; 60° C., 1.4580	...	24.2-31	18-28
Cotton-seed oil	$\frac{15.5}{15.5}$ 0.920-0.928; ($\frac{15}{15}$ 0.930)	...	...	15° C., 1.475; 60° C., 1.4586	$\frac{100}{100}$ 0.8816	35-40	32-38
Rape-seed oil	$\frac{15.5}{15.5}$ 0.912-0.917	...	− 1 to − 10	15° C., 1.4745; 60° C., 1.4584	$\frac{100}{100}$ 0.8758	17-21	12-16.5
Black mustard oil	$\frac{15.5}{15.5}$ 0.915-0.919	...	− 17.5	40° C., 1.4655	...	16-17	15
White mustard oil	$\frac{15.5}{15.5}$ 0.912-0.915	...	− 8 to − 16	40° C., 1.4649	...	15-16	...

Non-drying oils and solid fats—							
Earth-nut oil	$\frac{15.5}{15.5}$ 0.916-0.9256	...	− 3 to − 7	15° C., 1.4731; 60° C., 1.4564	$\frac{100}{100}$ 0.8475-0.864	27-32	22-30
Almond oil	$\frac{15.5}{15.5}$ 0.917-0.9195	...	− 10 to − 21	25° C., 1.468-1.467; 60° C., 1.4555	...	14	5-14
Croton oil	15° C., 0.940-0.960; 100° C., 0.8874	...	− 16	27° C., 1.4768	...	...	16.4-19
Grape-seed oil	15° C., 0.920-0.596	..	− 10 to − 17	...	...	23-25	18-20
Castor oil	$\frac{15.5}{15.5}$ 0.960-0.967	...	− 10 to − 18	15° C., 1.4803; 60° C., 1.4647	...	13	3
Olive-kernel oil	$\frac{15}{15}$ 0.918-0.920	...	...	1.4682-1.4688	...	...	...
Olive oil	$\left(\frac{15}{15}\right.$ 0.914) $\frac{15.5}{15.5}$ 0.917-0.920 $\frac{100}{100}$ 0.862-0.864	...	...	15° C., 1.4718; 60° C., 1.4546	$\frac{60}{15}$ 0.878; $\frac{100}{100}$ 0.8749	22-26	21-24
Ben oil	$\frac{15}{15}$ 0.9120	...	...	...	...	...	...
Neat's foot oil	$\frac{15}{15}$ 0.914-0.919	...	...	15° C., 1.473; 60° C., 1.4559	$\frac{100}{100}$ 0.8742-0.8800	28-30	16-26.5
Lard	$\frac{15}{15}$ 0.931-0.938 $\frac{60}{15.5}$ 0.886 $\frac{100}{15}$ 0.860-0.862	40-45	27-30	40° C., 1.458-1.460; 60° C., 1.452	...	35-45	37-39
Lard oil	$\frac{15.5}{15.5}$ 0.917 100°, 0.8626	...	...	...	0.885	35	31
Mahwa butter (*Bassia latifolia*)	$\frac{100}{100}$ 0.8943-0.8975	23.0-31.0	19-22	40° C., 1.4605-1.4609	...	45	40
Mowrah seed oil (*Bassia longifolia*)	100° C., 0.8854	35.5-42	25-36	...	...	54 5-55.5	52.5
Palm oil	$\frac{60}{15.5}$ 0.8837 $\frac{100}{100}$ 0.858	...	...	60° C., 1.451	$\frac{100}{100}$ 0.870	47-50	40-45
Bone fat	$\frac{15.5}{15.5}$ 0.914-0.916 $\frac{60}{15.5}$ 0.894	21-22	...	60° C., 1.451	...	30-42	28-32

The Physical Properties of the Oils, Fats, and Waxes (*continued*)

	Specific Gravity.	Melting Point.	Solidifying Point.	Refractive Index.	The Insoluble Fatty Acids		
					Specific Gravity.	Melting Point.	Solidifying Point.
Non-drying oils and solid fats (*cont.*)		° C.	° C.			° C.	° C.
Tallow (beef)	$\frac{60}{15.5}$ 0.901, $\frac{100}{100}$ 0.860	42-48	...	40° C., 1.4987 60° C., 1.442	...	45-47	42.5-45
Tallow (mutton)	$\frac{60}{15.5}$ 0.907	47-51	...	60° C., 1.4531	...	45-50	43-46
Tallow oil	$\frac{100}{100}$ 0.794	...	...	...	...	...	35-37.5
Cocoa (cacao) butter	$\frac{100}{100}$ 0.903-0.904	23.5-33	...	40° C., 1.448-1.458 60° C., 1.450-1.458	...	45-51	47.2-49.2
Vegetable tallow	...	37-46	24-31	...	...	40-57	34-48
Butter fat	$\frac{40}{15.5}$ 0.904-0.9102 $\frac{100}{15}$ 0.865-0.870 $\frac{100}{100}$ 0.909-0.914	29-34.6	19-20	25° C., 1.459-1.462 60° C., 1.445-1.450	$\frac{20}{20}$ 0.9106-0.9242	38-43	...
Palm-kernel oil	$\frac{60}{15.5}$ 0.896, $\frac{99}{15}$ 0.873	23-28	...	40° C., 1.450 60° C., 1.443	...	21-28	...
Japan wax	$\frac{60}{15.5}$ 0.902-0.907 $\frac{98}{15.5}$ 0.875	42-45	...	60° C., 1.450	...	56-57	53-56.5
Myrtle wax	$\frac{98}{15.5}$ 0.875	40-44	39-5-43	...	$\frac{99}{15.5}$ 0.837	47.5	46.0
Cocoa-nut oil	$\frac{60}{15.5}$ 0.897, $\frac{99}{15.5}$ 0.874	...	...	40° C., 1.445-1.450 60° C., 1.442	...	24-27	19-23
Marine animal oils—							
Menhaden oil	$\frac{15.5}{15.5}$ 0.932-0.935	...	−4	...	...	...	...
Sardine oil	$\frac{15}{15}$ 0.925-0.928 $\left(\frac{15}{15}\right)$ 0.916-0.933)	20-22	...	15° C., 1.479	...	30-31	...
Cod-liver oil	$\frac{15.5}{15.5}$ 0.922-0.935	...	...	15° C., 1.482 60° C., 1.462-1.466	$\frac{60}{60}$ 0.882	21-25	...

Seal oil	$\frac{15}{15}$ 0.924-0.927	—	—	15° C., 1.478 60° C., 1.4619	—	...	...
Whale oil	$\frac{15}{15}$ 0.920-0.927	—	...	15° C., 1.476 60° C., 1.460	—	...	...
Porpoise oil	$\frac{15}{15}$ 0.926-0.927	...	−16	...	...	...	...
Dolphin oil	$\frac{15}{15}$ 0.918	...	...	...	...	...	...
Liquid waxes—							
Sperm oil	$\frac{15.5}{15.5}$ 0.875-0.886	...	...	15° C., 1.467 60° C., 1.4508	$\frac{15}{15}$ 0.899	13.3	...
Arctic sperm (bottlenose) oil	$\frac{15.5}{15.5}$ 0.880	...	...	...	...	10.3-10.8	...
Solid waxes—							
Spermaceti	$\frac{98}{15.5}$ 0.808-0.816	43-49	42-45	...	...	...	...
Beeswax	$\frac{15}{15}$ 0.961-0.970	62-65	...	...	...	...	...
Carnaüba wax	$\frac{15}{15}$ 0.99-1.0	83-86	...	...	...	...	...
Wool wax	$\frac{15}{15}$ 0.973, $\frac{60}{15.5}$ 0.885	36-43	...	60° C., 1.465	...	41.8	40

NOTES

It has not been thought necessary to quote the authorities for the figures in this table.

Figures in brackets represent abnormal results, possibly due to the examination of a genuine oil of unusual character, or of a sample which has undergone modification through keeping.

as well as the potassium salts of several fatty acids.—Sp. gr. 0.943 (17° C.), 0.90 at 100° C.; sol. pt. 30°; M.P. 36°-42° C.; refract. index (60° C.) 1.465; sap. val. 80-100; iod. val. 20-29; fatty acids, 60 per cent.; alcohols, 43-50 per cent. Mixed fatty acids melt 41° C.; iod. val. 17; mol. wt. 327. Mixed alcohols, M.P. 33° C.; iod. val. 26-36; acetyl. val. 144; mol. wt. 239.

Pure Lanolin is perfectly neutral, does not become rancid, and is very difficult to saponify; its capacity for absorbing water is most remarkable, taking up when kneaded 110 per cent. to form a cream; it similarly takes up glycerin. The skin absorbs it in an extraordinary way, and thus it serves as an excellent basis for introducing effective remedies through the skin; for instance a lanolin corrosive sublime ointment containing but $\frac{1}{1000}$ per cent. of corrosive sublimate produces a metallic taste upon the tongue within a few minutes of application to any part of the body! Lanolin consequently forms an excellent basis—either hydrated or combined with glycerin—for ointments, pomatums, and cosmetics.

Distilled Grease

Yorkshire grease from wool and soap suds is often too dirty and odoriferous to be used for anything except cart grease and rough lubricating materials for rollers, etc. To obtain a better product it is often distilled in cast-iron stills holding about 4 tons of grease, first for ten to sixteen hours over a free fire (to remove water), and then for twenty to twenty-four hours with superheated steam.

"**Spirit Oil**" (*sometimes*, not *always*) comes over first. Pale yellow oil, darkens on keeping, boils over at 150°-320° C. Used in making black varnish.

First Distilled Grease is the second product coming over. It is often allowed to crystallise, and is then pressed for liquid **oleic acid** and solid "**stearine**" (M.P. 48°-57° C.). It is sometimes redistilled ("**second distilled grease**").

The next product to distil is the "**green oils**," sometimes used for coarse lubricating greases; more often mixed with another batch of material and redistilled.

Pitch remains behind in the still. It is used as a lubricant for the necks of hot rollers.

Wright gives the following numbers for the distillation of 100 parts Yorkshire grease:—Pitch, 14 per cent.; green oil, 15.5 per cent.; first distilled grease, 45.5 per cent.; spirit oil, 4 per cent.; water and loss, 21 per cent. Lewkowitsch finds in distilled grease 55 per cent. free fatty acids; 7 per cent. combined fatty acids; 39 per cent. unsaponifiable matters.

Solid Vegetable Waxes.

Carnaüba Wax is exuded by the leaves of the Brazilian wax palm, *Corypta cerifera*, and consists principally of myricyl cerotate. Used in candle manufacture, polishing pastes (wax varnishes), and in making phonograph cylinders.—M.P. 84° C.; acid val. 4-8; sap. val. 79-95; iod. val. 13. True acetyl. val. 55; sp. gr. (15° C.), 0.99-1.0, 0.84 at 100°.

Other vegetable waxes are flax wax, gondang wax, pisum wax, opium wax, palm wax, ocuba wax, cotton-seed wax.

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IV.—METHODS OF EXAMINATION OF FATTY OILS

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LITERATURE

See under Animal and Vegetable Fatty Oils.

Methods of Examination.—Only in exceptional cases (such as sesamé oil and cotton-seed oil, which contain characteristic compounds) is it possible to directly identify a given fatty oil by means of a reagent, and it is therefore necessary to apply physical and chemical tests, which will locate the oil in successively narrowing groups and finally to apply similar tests of identity.

The methods employed include a determination of the so-called "constants" or values of the sample, such as the specific gravity, solidification and melting points, optical properties, amount of iodine absorbed (iodine value), amount of alkali required for saponification (saponification value), amount of volatile and insoluble fatty acids present in the oil (Reichert and Hehner values), etc.

The difficulty of the task is often increased by the fact that oils and fats of the same kind show considerable variations in their constants—so much so that an oil—*e.g.*, olive oil—may contain a considerable proportion of an adulterant such as maize oil, and still show values falling within the higher limits recorded for the pure natural oil. This will be seen more clearly in the following details concerning the "values."

Specific Gravity.—This is usually determined at a temperature of 15.5° C. in the case of oils and at 100° C. in the case of solid fats, water at 15.5° C. being taken as unity. *Tables of Specific Gravities* are given, pp. 56-59.

The following table, based on a system first proposed by Allen, illustrates the assistance given by the specific gravity in the classification of oil.

Oils.

Sp. gr. 0.913-0.920 (15.5° C.).	Sp. gr. 0.920-0.925 (15° C.).	Sp. gr. 0.925-0.935	Sp. gr. 0.935-0.960 (15.5° C.).
Almond oil. Colza ,, Arachis ,, Olive ,,	Cotton-seed oil. Maize ,, Sesamé ,, Cod-	Linseed oil. Whale ,, ... Liver oil.	Tung oil. Castor ,, Croton ,, ...

Fats and Waxes.

Sp. gr. 0.800-0.855 (100° C.).	Sp. gr. 0.855-0.863 (100° C.).	Sp. gr. 0.863-0.867 (100° C.).
Spermaceti. Bee wax.	Palm oil. Cacao butter. Tallow. Lard.	Cocoa-nut oil. Japan wax. Butter fat. ...

Refractive Index.—Oils frequently show pronounced differences in their refractive index—so much so that this value when determined by means of a refractometer at a definite temperature may afford decisive proof of adulteration. Thus in the case of butter fat Wollny obtained readings varying from 1.4560-1.4620, while margarine gave readings of 1.4650-1.4700, and mixtures of butter and margarine readings of 1.4620-1.4690.

A special instrument termed a "butyro-refractometer," in which the readings are given in degrees on a scale, is widely employed for this purpose, and is particularly useful as a sorting test. As is evident, however, from the examples quoted above, a mixture of butter with a small percentage of margarine may give refractometer readings falling within the limits of those of genuine butter. (See *Tables*, pp. 56-59.)

Melting and Solidification Points.—The temperatures at which fats or oils melt or solidify also afford means of identifying different samples. For instance, almond oil does not solidify until chilled to −20° C., whereas olive oil solidifies at about 2°-4° C. These differences largely depend upon the nature of the fatty acids in the glycerides. Thus olive oil contains a large proportion of the glycerides of solid fatty acids, whilst in almond oil such glycerides are only present in traces, the oil consists chiefly of glycerides of liquid fatty acids. (See *Tables*, pp. 56-59.)

The melting points of the separated fatty acids may also afford valuable information. The following are a few solidifying points of fatty acids obtained from various oils and fats (the numbers represent Centigrade degrees):—

Beef tallow, 38-46.
Mutton tallow, 41-48.
Lard, 34-42.
Horse fat, 33.7.
Neat's foot oil, 26.5.
Palm oil, 36-45.
Cocoa-nut oil, 20-25.
Palm-nut oil, 20-25.
Japan wax, 59.
Vegetable tallow, 45-53.
Linseed oil, 13-17.
Tung oil, 37.
Hemp oil, 14-16.
Poppy-seed, 16.5
Cotton-seed, 32-36.
Rape, 12-18.
Olive, 17-26.
Arachis, 23-29.
Cod-liver, 18-24.
Whale, 24.
Japanese sardine, 28.

The **Acid Value.**—This is a measure of the quantity of potassium hydroxide required to neutralise the free fatty acids in an oil. Gradual decomposition of the glycerides into their components glycerol and free fatty acids takes place when a fat is exposed to the action of light and air, with the result that the acid value steadily rises. This value may therefore be a test of the freshness of an oil. Old and rancid fats sometimes have very high acid values. (See *Table*, p. 54.)

Saponification Value.—The oil is boiled with a measured excess of alkali in suitable solution, and the amount (expressed in milligrammes of potassium hydroxide) required to effect complete decomposition of one gramme of the fat into soap and glycerol or other alcohol is termed the saponification value.

As the fatty acids possess different molecular weights, the proportion of alkali required to neutralise them will also vary, and the oils containing them will have different saponification values. (See *Tables*, pp. 54, 55.)

By way of example, the following saponification values may be quoted:—

Castor oil, 176-183.
Cod-liver oil, 182-187.
Cotton-seed oil, 192-193.
Olive oil, 190-195.
Linseed oil, 190-195.
Almond oil, 190-192.
Lard, 195-196.
Butter fat, 225-230.
Cocoa-nut oil, 255-260.
Beeswax, 90.
Paraffin wax, 0.
Wool wax, 102.
Insect wax, 90.
Spermaceti, 123-134.
Sperm oils, 123-136.

Hence, if a sample of lard showed a saponification value of, say, 200, the presence of cocoa-nut oil would be suggested and further tests for that fat would be applied.

NOTE.—(1) Waxes, both liquid and solid, are characterised by such low saponification values that they are easily distinguished by this means from oils.
(2) The majority of oils and fats have saponification values about 193. Higher or lower values than this may suggest the presence of special oils.
(3) Mineral oils have a zero saponification value, and consequently their presence lowers the saponification value of a fatty oil.

Iodine Value.—The liquid fatty acids, which form the principal constituent of the glycerides in fluid oils, are unsaturated compounds, and will combine with bromine or iodine (in suitable form) to form saturated bodies. The percentage of iodine absorbed in this test is termed the iodine value, and is a most valuable means of identifying different groups of oil.

One class of oils, typified by almond and olive oils, consists largely of oleic acid (which absorbs approximately 90 per cent. of iodine). These have iodine values of about 80-95, and are known as **non-drying oils.**

Another group contains oils in which linolic acid (absorbing about 181 per cent. of iodine) is an important constituent. Cotton-seed oil (iodine value, about 108), sesamé oil (iodine value, 110), and maize oil (iodine value 120) are examples of these oils, which are termed **semi-drying oils.**

A third important group contains the **drying oils,** in which the glyceride of linolenic acid (iodine value, 274) is usually an important constituent. They naturally have high iodine values, *e.g.*, linseed oil, 195; nut oil, 142.

Marine animal oils also have high iodine values, due to the presence of highly unsaturated fatty acids, but they may be distinguished from drying oils by their non-drying properties, and by other tests.

Solid fats have iodine values which are greater in proportion to the amount of unsaturated fatty acids they contain. Lard, for instance, usually has an iodine value of 50-60, so that a high iodine value (*e.g.*, 70) points to the lard having been stiffened with beef fat, and then rendered sufficiently fluid again by the addition of a vegetable oil, such as maize or cotton-seed oils.

Certain kinds of American lard, however, normally have high iodine value (up to 66), and it is therefore necessary to confirm the presence of a vegetable oil in lard by other tests (see p. 66).

IODINE VALUES OF COMMON OILS, FATS, AND WAXES (see p. 55)

Oleic acid, 90.	Sunflower oil, 118-136.
Tallow, 35-46.	Hemp-seed oil, 140-166.
Butter, 36-48.	Poppy-seed oil, 137-143.
Lard, 50-65.	Walnut oil, 143-148.
Mutton fat oil, 32-57.	Seal oil, 127-146.
Oleo margarine, 53-88.	Whale oil, 121-146.
Olive oil, 79-93.	Cod-liver oil, 154-181.
Sesamé oil, 103-112.	Shark liver, 115.
Rape oil, 94-108.	Menhaden oil, 175-183.
Cotton-seed oil, 105.	Sardine oil, 161-193.
Castor oil, 83-86.	Porpoise oil, 131.
Arachis oil, 90-103.	Sperm oil, 81-84.
Palm oil, 51-57.	Arctic sperm oil, 67-82.
Cocoa-nut oil, 8-9.	Insect wax, 1.4.
Palm-kernel oil, 10-17.	Beeswax, 10.
Croton oil, 101-109.	Spermaceti, 4.
Linseed oil, 179-200.	Wool wax, 17.
Tung oil, 149-167.	Carnaüba wax, 13.

NOTES.—(1) Linseed oil has a high iodine value, and adulteration with foreign oils lowers that value.

(2) The addition to walnut or poppy-seed oil of 5-10 per cent. of rape or cotton-seed oils and 20 per cent. linseed has an influence on the iodine value.

(3) The adulteration of olive oil with only 5 per cent. of a drying oil and 15 per cent. of cotton seed, sesamé, rape, or arachis oil may be suggested by the iodine value.

(4) Fish oils have very high iodine values, and their presence is thus indicated in oils with low iodine values but not in drying oils.

(5) If I denotes the iodine value of a mixture of two fats whose iodine values are m and n respectively, then, **percentage of fat** $m = \frac{100(I-n)}{m-n}$.

Hehner Value.—This test devised by Hehner indicates the percentage of insoluble fatty acids which can be separated from an oil or fat. It is usually about 93-96, but in the case of fats (such as butter, cocoa-nut oil, and palm oil) which contain a high proportion of volatile and soluble fatty acids it is much lower. Thus butter usually has a Hehner value ranging from 85-88, and cocoa-nut oil a value of 88-90.

We give a few numbers; for others see *Table*, p. 54:—

100 g.	**cow's butter fat**	contain	86-89	g.	insoluble fatty acids.
,,	tallow	,,	96	,,	,,
,,	lard	,,	96	,,	,,
,,	olive oil	,,	95	,,	,,
,,	poppy seed	,,	95	,,	,,
,,	palm oil	,,	96	,,	,,
,,	palm kernel	,,	91	,,	,,
,,	cocoa-nut oil	,,	89	,,	,,
,,	dolphin jaw oil	,,	66	,,	,,
,,	porpoise jaw oil	,,	70	,,	,,

Reichert Value.—This is a measure of the amount of alkali expressed in c.c. of decinormal solution, required to neutralise the proportion of volatile soluble fatty acids liberated and distilled under the constant conditions laid down by Reichert. A modification of the method devised by Meissl is more commonly employed, the value being termed the **Reichert-Meissl** value, and relating to 5 g. instead of 2.5 g. of the fat. The following are a few typical Reichert-Meissl values (for others see *Table*, p. 56):—

Butter fat, 28 c.c. (24-33).	Cocoa-nut oil, 7-8 c.c.
Beef tallow, 0.5 c.c.	Maize oil, 0.3-4.4 c.c. (Reichert).
Olive oil, 0.6 c.c.	Croton oil, 13 c.c.
Sesamé oil, 0.7 c.c.	Dolphin oil, 11 c.c.
Rape oil, 1.0 c.c.	Dolphin jaw oil, 130 c.c.
Palm oil, 1.0 c.c.	Porpoise body oil, 46 c.c.
Palm-kernel oil, 5 c.c.	Porpoise jaw oil, 100-139 c.c.

Most of the solid animal body fats have only trifling Reichert-Meissl values, but in butter fats the proportion of volatile fatty acids is high, and correspondingly high values are obtained in the test.

Thus in the case of cow's butter the value normally ranges from about 24 to about 33. Hence when a sample of butter shows a Reichert value of, say, 20, the addition of an adulterant is probable. In the case of certain kinds of Dutch cows, however, the butter fats sometimes give a value as low as 17, this being attributed to leaving the herds in the fields too late in the season.

Most vegetable oils and fats have a Reichert-Meissl value of less than 2, but cocoa-nut oil has a value of 7-8, and palm-kernel oil a value of about 4. A considerable amount of these fats may, therefore, be added to butter without rendering the Reichert value suspiciously low.

Of late several methods of detecting these fats in butter have been based upon a separation of the fatty acids intermediate between the quite insoluble acids and those readily volatile. Cocoa-nut oil and palm-kernel oil are particularly rich in these acids, and therefore show an "extended" Reichert value, which is not given by butter. (See also pp. 75, 87.)

Maumené Test.—Weigh 50 g. of oil into a 200 c.c. tall beaker packed with cotton wool into a litre beaker; run in slowly (take sixty seconds) from a burette 10 c.c. of concentrated sulphuric acid, stirring continually with a thermometer; the highest temperature attained is the required value.

Olive oil, 42° C.
Almond oil, 52°-54° C.
Rape oil, 57°-60° C.
Arachis oil, 45°-75° C.
Sesamé oil, 68° C.
Cotton seed, 75°-90° C.
Poppy seed, 88° C.
Walnut, 101° C.
Hemp seed, 98° C.
Linseed, 103°-145° C.
Castor, 47° C.

Tallow oil, 41°-44° C.
Neat's foot, 48° C.
Cod liver, 102°-103° C.
Skate liver, 102° C.
Menhaden, 126° C.
Seal, 93° C.
Whale, 92° C.
Porpoise (body), 51° C.
Sperm, 51° C.
Arctic sperm, 41°-47° C.

Drying oils have a high Maumené value; so also have fish oils. Non-drying oils have a low value.

Elaïdin Test.—Useful for detecting drying oils mixed with non-drying, and *vice versâ*. Measure 50 c.c. of oil into a wide-mouthed stoppered bottle of 100 c.c. capacity; add 2 c.c. of cold, freshly-made mercury nitrate (prepared by dissolving 13 g. mercury in 12 c.c. concentrated nitric acid, keeping cold in cold water to retain nitrous fumes), shake well; place in air oven at 25° C. for twenty-four hours, agitating from time to time; simultaneously perform a comparison experiment with a standard sample of oil, and compare results. Note length of time of solidification and consistency of mass after twenty-four hours.

Drying Oils (linseed, hemp seed, walnut, poppy, etc.) remain *fluid*.

Semi-drying Oils (rape, neat's foot, sperm, cotton seed, etc.) yield after twenty-four hours a thick mass of treacle-like consistency.

Non-drying Oils (olive, sperm, tallow, etc.) turn into a solid mass.

The following examples show the use of these constants in analytical work.

1. A sample of oil sold as olive oil had the following characteristics: Sp. gr. 0.924; acid value, 4; saponification value, 190; iodine value, 105; refractometer reading, 67; melting point of fatty acids, 24° C.

The iodine value at once indicated that this was not pure olive oil, and the other values agreed with those of pure sesamé oil. This was confirmed by a special colour reaction for that oil, and by the fact that it slowly dried on exposure in a thin film to the air.

2. A solid fat sold as lard gave the following results: Iodine value, 72; and Reichert-Meissl value, 2.5. The high iodine value suggested the presence of a vegetable oil, and this was found by special colour reactions to be cotton-seed oil. The Reichert-Meissl value indicated the presence of cocoa-nut oil, and this was confirmed by other tests.

Differentiation of Fish Oils from Drying Oils.—Oils such as cod-liver oil (and marine animal oil, whale, etc., in general) may be distinguished from linseed and other drying oils by drying tests, and by the fact that on treatment with bromine they yield an insoluble white compound, which turns black when heated.

The corresponding compound from linseed oil treated in the same way melts to form a colourless liquid. *The following list gives the percentage yield of* insoluble bromides *from certain typical oils:* *—

Linseed, 24-38.
Tung oil, *nil.*
Candle-nut oil, 8.
Walnut oil, 1.4-1.9.
Poppy-seed oil, *nil.*
Maize oil, *nil.*
Cotton-seed oil, *nil.*
Brazil-nut oil, *nil.*
Olive oil, *nil.*

Almond oil, *nil.*
Fish oil (deodorised), 50.
Cod-liver oil, 30-43.
Japan fish oil, 22.
Shark liver, 20.
Seal oil, 28.
Whale oil, 15-26.
Sperm oil, 2.4-3.7.

Mineral Oils in Fatty Oils.—In order to detect **mineral oils, paraffin wax**, and other unsaponifiable matters in fats, we proceed thus: Saponify with alcoholic potash, evaporate to dryness on

* This test was originated by C. A. Mitchell. Lewkowitsch and others invariably describe these insoluble bromides as "hexabromides." They are the bromides of mixed glycerides and certainly not hexabromides.

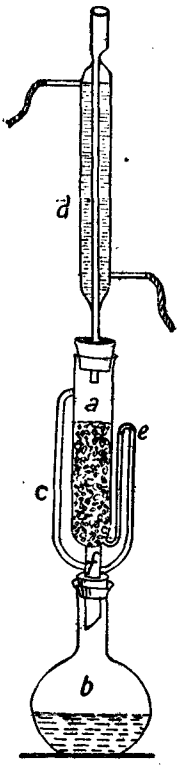

FIG. 20.—Soxhlet Fat Extraction Apparatus.

the water bath, extract the unsaponifiable matter with petroleum spirit or ether, evaporate the solvent, and the residue represents the amount of unsaponifiable matter. *The saponification is effected thus:* Weigh out 10 g. fat into a porcelain basin, add 50 c.c. of 8 per cent. alcoholic potash solution, boil on water bath until soap begins to froth, then add 15 c.c. alcohol and boil until the soap is dissolved. Stir into the mass 5 g. sod. bicarbonate and 50-60 g. recently ignited pure white sand; dry twenty minutes in water oven, transfer to a Soxhlet apparatus, extract with petroleum spirit (B.P. below 80° C.), distil off petroleum spirit and weigh residue. **Waxes** require prolonged boiling for complete saponification, but are more easily saponified if boiled with a freshly-made solution of sodium (5 g.) in absolute alcohol (100 c.c.). The Soxhlet apparatus used for extraction is shown in the figure. The substance to be extracted is placed in the tube *a*, which is closed at *f*. In *b* petroleum spirit is placed and heated to boiling point. The vapour rises through *c* into the condenser *d*, and, descending in the form of drops, gradually fills *a* with liquid to the level of the bend in the tube *e*; when this happens, the liquid syphons over into the flask *b*, bearing with it the extracted matter. Then the process begins anew, a continual stream of solvent flowing through *a* until all the extractible matter is removed from the substance. The fluid in *b* is then distilled, and the extracted matter remaining behind is dried at 100° and weighed.

To Distinguish Between Animal and Vegetable Oils and Fats

Animal Oils and fats contain the alcohol **cholesterol**, $C_{27}H_{46}O$. **Vegetable fats** contain a similar alcohol called **phytosterol**, $C_{29}H_{48}O$. This fact allows us to distinguish between animal and vegetable fats. If the fat contains *both* cholesterol and phytosterol it is a mixture of animal and vegetable fats. The method of examination is as follows: Saponify a considerable quantity of fat by alcoholic potash; the cholesterol or phytosterol remains in the unsaponifiable matter. If the body is a wax, saponify with sodium dissolved in absolute alcohol.

1. Dissolve the unsaponifiable matter in ether, filter if necessary, evaporate off the ether, redissolve in absolute alcohol, and allow to crystallise on a watch glass; examine crystals under the microscope. Crystals of cholesterol have a different shape from those of phytosterol.

2. Heat crystals obtained in 1 with 2·3 c.c. of acetic anhydride in a small dish covered with a watch glass; evaporate off the acetic anhydride on the water bath and crystallise twice from alcohol. Take melting point in the usual way.

Cholesteryl acetate melts 114°-115°; **Phytosteryl acetate** melts 125°-137° C. Hence they are easily distinguished.

If both cholesteryl and phytosteryl acetates are present fractionally crystallise the mixture several times from alcohol and thus separate the crystals into high melting and low melting portions, and examine these separately.

V.—MILK, BUTTER, AND CHEESE INDUSTRY

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MILK

The average composition of cow's milk may be taken to be: Water, 87.60; protein, 3.50; fat, 3.40; milk sugar, 4.60; mineral matter or ash, 0.75.

In addition to the above, milk contains small quantities of other substances. Some of these, such as lecithin and nuclein, have an important physiological value, whilst others like urea, cholesterine, hypoxanthine are unimportant.

Milk being a liquid designed for the nutrition of the young contains those materials needed for the development and growth of the organism in its early stages. The proportions in which the various constituents are present in human milk and in the milk of different animals varies somewhat widely, as will be seen from the following table:—

	Woman.	Cow.	Goat.	Sheep.	Horse.	Ass.
Water	88.32	87.75	86.34	81.08	90.38	90.35
Fat	3.43	3.40	4.25	7.67	1.00	1.30
Protein	1.55	3.50	4.40	6.08	1.98	1.80
Milk sugar	6.44	4.60	4.26	4.26	6.28	6.20
Salts	0.26	0.75	0.75	0.91	0.36	0.35
	100.00	100.00	100.00	100.00	100.00	100.00
Specific gravity	1.032	1.0315	1.033	1.038	1.034	1.033

Comparison of the composition of human milk and other milks will show that considerable differences exist. For the feeding of infants this point is worth attention.

Confining all further remarks to the milk of the cow, it may be said that fresh milk is homogeneous with a bluish yellow colour. The colour varies according to the breed of the cow, Channel Island cattle giving a milk which has a much deeper yellow tint than the milk of other breeds.

Milk has a pleasant, sweetish taste and a characteristic animal smell, but this should not be markedly noticeable. The smell, in fact, may be absent if the milk has been obtained under conditions of extreme care and cleanliness.

When tested with litmus paper milk shows a distinct amphoteric reaction, that is, it turns red litmus paper blue, and blue litmus paper red. The presence in the milk of various neutral and acid phosphates of potassium and calcium as well as carbonates of these two metals causes this reaction. To phenolphthalein milk is acid.

The average specific gravity of milk may be taken to be 1.0315. The freezing point lies below that of pure water, viz. −0.553° C., and the boiling point about 0.2° C. higher than water.

Milk when left to stand throws up a layer of cream owing to the rise of the specifically lighter fat globules. In the milk of some breeds of cattle the fat globules are considerably larger than the average, and so rise more quickly. According to Gutzeit the average diameter of the globules in the milk of the shorthorn is 2.76 μ, whilst in the Jersey it is 3.5 μ.

As regards the number of fat globules in a cubic millimetre of milk varying results have been obtained—average figures are difficult to give, but probably three to five millions is not far wrong.

It has been held by some authorities that the globules of fat are surrounded by some membrane which keeps them apart. This membrane is variously stated to be composed of fibrin, globulin, or casein, whilst Storch isolated from cream, that had been repeatedly washed with water, a material containing 14.77 per cent. of nitrogen which he considered came from the "mucoid membrane" surrounding the fat globules.

The ordinary laws of surface tension seem, however, to satisfactorily explain how the globules are kept apart, and at the present time this is the prevalent view. The work of Morres* gives strong support to this view.

Considering in detail the constituents of the dry matter, or total solids of milk, the first important class is that of the proteins. There are three of these—casein, albumin, and globulin, and the first represents about 85 per cent. of the total protein of milk. The albumin and the globulin make up the remaining 15 per cent., the latter only being present in very small quantities.

Casein is an interesting chemical substance of great economic value; in fresh milk it is in suspension in a finely divided colloidal state. It cannot be separated by filter paper, but filtration through an unglazed earthenware filter leaves the casein (and fat) as a porcelain-like mass on the sides of the filter. This shows that the casein is not dissolved in milk, but is suspended.

The casein from cow's milk is very similar to, although perhaps not identical with, the casein of the milk of other animals.

What is ordinarily called the casein of milk appears to be a compound of casein (which may be regarded as an acid having a basicity of four or six) with lime. The compounds of casein with the alkalies give solutions which are almost clear, with, at the most, a faint opalescence.

Up to the present three compounds of lime and casein have been described, the monocalcium with 0.87 per cent. CaO, the dicalcium with 1.55 per cent. CaO, and the tricalcium with 2.46 per cent. CaO. The existence of the mono- and tricalcium caseinates has been questioned.

Casein is a nucleo-albumin which is distinguished from others of its class by

* *Milchwirtschaft Zentralblatt*, 1909, p. 502.

the amount of phosphorus which it contains, and by the effect which rennet has upon it.

The elementary composition of the casein of cow's milk can be seen from the following analyses:—

	Hammarsten.	Tangl.	Burow.	Ellenberger.	Duclaux.
C	52.96	52.69	52.825	53.07	53.00
H	7.05	6.81	7.095	7.13	7.00
O	...	23.141	22.906	22.60	22.65
N	15.65	15.65	15.640	15.64	15.70
P	0.847	0.877	0.808	0.80	0.85
S	0.758	0.832	0.725	0.76	0.80

When milk is acted upon by an acid, or when it sours spontaneously, the casein lime compounds are split up and free casein is precipitated in the form of curd. It appears as though the casein combines with stronger acids, in other words, behaves like a weak base. Van Slyke and Hart describe a casein lactate which they found in sour milk, and similar acid casein compounds are said to arise by the action of organic or mineral acids. More recent work, however, throws doubt upon some of these acid casein compounds. The curdling of milk by rennet may be regarded as taking place in two stages. First the enzyme of rennet splits up the lime casein compounds into paracasein and whey albumin, and coagulation then follows if lime salts are present. The paracasein forms the curd, the whey albumin remains in the whey.

There is thus a fundamental difference between the curd obtained when the milk is coagulated by rennet, and when this takes place under the influence of acids.

The **Albumin** of milk was prepared by Sebelien in a pure state from whey by saturation with magnesium sulphate. It is very similar to blood serum, but has a less specific rotation—$a_D = -37°$ as compared with $a_D = -57°$ to $-64°$ for blood serum.

Albumin is soluble in cold water, and coagulates at a temperature of 70°-72° C.

In **Colostrum**, the milk which is given immediately after calving and for several days following, a large percentage of the protein is albumin. Immediately after the birth of the calf the colostrum may contain as much as 16 per cent. of albumin, and this quantity diminishes until after about seventy-two hours the milk again reaches its normal composition. This is shown in a series of analyses by Eugling.

	Number of Hours after Calving.					Ordinary Milk.
	Immediately After.	10 Hours.	24 Hours.	48 Hours.	72 Hours.	
Water	73.17	78.77	80.63	85.81	86.64	87.75
Casein	2.65	4.28	4.50	3.25	3.33	3.00
Albumin + Globulin	16.56	9.32	6.25	2.31	1.03	0.50
Fat	3.54	4.66	4.75	4.21	4.08	3.40
Milk sugar	3.00	1.42	2.85	3.46	4.10	4.60
Ash	1.18	1.55	1.02	0.96	0.82	0.75

As already mentioned, only traces of globulin are present in milk.

Fat.—Attention has already been directed to the characteristic globules in which the fat of milk is found. The fat itself is of a pale yellow colour, and is characterised chemically by the glycerides of lower fatty acids which it contains,

and physically by its undercooled state. Upon the chemical properties are based many of the methods used in the analysis of butter. The undercooled condition of the fat is seen when cream is made into butter, for then the solid fat is obtained. The melting point of butter fat lies between 31° and 36° C. and the sp. gr. is 0.93 at 15° C., a fact which accounts for the rising of the fat globules when milk is left to stand.

Milk Sugar is the only carbohydrate of importance in milk. See pp. 78*a*, 78*b*.

Small quantities of other carbohydrates have from time to time been said to be present also, but their presence lacks confirmation. Milk sugar is a biose, it crystallises with 1 molecule water, and can easily be obtained from whey. Milk sugar is not as sweet as cane sugar, nor is it so soluble in water; 1 part dissolves in 6 parts cold water or 2½ parts hot water. Milk sugar differs further from cane sugar in not being fermentable with ordinary yeast; it can, however, undergo alcoholic fermentation when a yeast such as that found in "Kephir grains" is used.

Milk sugar reduces Fehling's solution, 0.1 gr. of the sugar being equivalent to 1.48 c.c. of Fehling's solution. It is also optically active, and fresh solutions show multirotation. See under **Sugar.**

Lactic Acid Fermentation.—A very typical fermentation which milk sugar undergoes is the lactic acid fermentation. This is brought about by the specific lactic acid bacteria. When the percentage of lactic acid reaches a certain point, *i.e.* 0.75-0.8 per cent., the development of the bacteria ceases. Before this point is reached the casein is coagulated and the milk, in ordinary language, is sour.

The Mineral Matter or Ash contains the salts left after ignition of the milk. As the process of ignition has caused the original milk salts to undergo changes it is difficult to say exactly in what form the salts were originally present in the milk. A comparison of the analysis of the ash of milk (by Schrodt and Hansen) and Söldner's arrangement of the salts of milk in the form in which he judges them to be present, will show the main characteristics.

Ash of Milk (Schrodt and Hansen).

K_2O	25.42	Fe_2O_3	0.11
Na_2O	10.94	SO_3	4.11
CaO	21.45	P_2O_5	24.11
MgO	2.54	Cl	14.60

Milk Salts (Söldner).

Sodium chloride	10.62 per cent.
Potassium chloride	9.16 ,,
Monopotassium phosphate	12.77 ,,
Dipotassium phosphate	9.22 ,,
Potassium citrate	5.47 ,,
Dimagnesium phosphate	3.71 ,,
Magnesium citrate	4.05 ,,
Dicalcium phosphate	7.42 ,,
Tricalcium phosphate	8.90 ,,
Calcium citrate	23.55 ,,
Lime combined with the casein	5.13 ,,

The presence of citric acid in milk was proved by Henkel, the quantity being about 0.10-0.15 per cent. The sulphuric acid in the ash comes from the sulphur of the casein and other proteins.

Analysis of Milk.—In the sample to be analysed, the fat globules must be evenly distributed through the liquid by vigorous mixing. If the cream has already separated the mixing may be brought about by warming to 40° C. and vigorous shaking.

The thoroughly mixed sample, kept sweet if necessary by the addition of a little formalin or powdered bichromate, is subjected to the following tests:—

1. The **Specific Gravity** is taken by means of a special hydrometer called a lactometer, or by a Westphal balance. Average sp. gr. = 1.0315.

2. The **Dirt** is estimated by settling in a long narrow vessel, filtering and weighing; or by filtering through cotton wool and judging the amount of dirt from the appearance of the filter afterwards.

3. The **Total Solids or Dry Matter** determined by evaporating a known quantity of milk to dryness in a flat porcelain or platinum dish, often with the addition of washed and ignited sand or pumice stone. The average weight of total solids = 12.25 per cent.

If the specific gravity G and fat content F of a milk are known, the total solids are given by the formula—

$$T = \frac{G}{4} + \frac{6}{5}F + .14.$$

4. **Fat.**—A great many analyses of milk are made for the fat alone; amongst the large number of methods used in the estimation of fat the following are to be recommended:—

(*a*) Adams' paper coil method, in which a known weight of milk is dried upon a strip of fat-free filter paper, and the paper, after drying, is extracted with ether in a Soxhlet apparatus.

(*b*) Röse-Gottlieb method. A mixture of ammonia and alcohol is used to dissolve the casein, and the fat is then shaken out with a mixture of ether and petroleum ether. Either the whole of the ether is evaporated and the fat weighed, or an aliquot portion of the ethereal solution is drawn off and evaporated.

(*c*) Gerber method. This is a modification of the Babcock test. It is accurate, and serves for separated milk if certain precautions are taken. Sulphuric acid (sp. gr. 1.82) is used to dissolve the casein, and to assist the separation of the fat amyl alcohol is added. On whirling the mixture of sulphuric acid, milk, and amyl alcohol in a specially constructed tube or butyrometer placed in a centrifuge, the fat separates out and can be read off on the scale placed upon the narrow part of the tube. 11 c.c. of milk, 10 c.c. of sulphuric acid, and 1 c.c. of amyl alcohol are the quantities used. The centrifuge must have a speed of 1,000 revolutions per minute, and this must be maintained for three or four minutes. In cold weather it may be necessary to warm the butyrometer tube, otherwise the column of fat solidifies, and cannot be read accurately.

Instead of sulphuric acid and amyl alcohol, both of which are objectionable, a mixture of common salt, sodium hydrate, and Rochelle salt takes the place of the acid, and isobutyl alcohol is used instead of amyl alcohol. This Sal method, as it is called, is quite satisfactory, but as no heat is generated by the mixing of the reagents, the butyrometer tube must always be warmed.

5. It is only exceptionally that the **protein**, the milk sugar, and the mineral matter are estimated in milk. The total protein can be determined by the usual Kjeldahl method, or more accurately by precipitation with copper hydrate (Ritthausen). Insoluble copper protein compounds are obtained, in which the nitrogen can be estimated.

6. **Milk Sugar** is estimated gravimetrically by weighing, either as CuO or Cu, the Cu_2O precipitated on boiling with Fehling's solution. The polariscope can also be used in the estimation of milk sugar, provided certain precautions are observed (*Scheibe, Milch Zeitung*, 1901, 113).

7. The **Ash or Mineral Matter** is extracted from the residue left after ignition. About 25 g. of milk are evaporated to dryness in a platinum dish, and then carefully ignited. As it is almost impossible to burn away all the carbon without volatilising some of the alkaline chlorides, etc., the ignited mass is extracted with water, filtered, and the residue well washed with warm water. The filtrate containing the milk salts is evaporated to dryness, gently ignited, and weighed. Should the ash of milk weigh less than 0.7 per cent., there would be grounds for suspecting the addition of water.

The Adulteration of Milk.—The removal of fat from milk, or the addition to it of water or separated milk, are the two chief adulterations practised. Further, milk to which the "strippings" have not been added may be regarded as adulteration, as is also the mixing of Pasteurised milk with fresh milk.

In this country the Board of Agriculture regulations for the sale of milk fix the minimum limit for butter fat at 3 per cent., and the solids not fat at 8.5 per cent. Milk that falls below these standards is regarded as not being genuine, and milk offered for sale and found to be below the above limits, renders the seller liable to a fine unless he can prove to the satisfaction of the authorities that the milk is genuine.

When the fat in genuine milk falls below 3 per cent., it may be due to various causes, *e.g.*, the length of intervals between milking, the season of the year, cold and wet weather, or insufficient food.

The production of milk on a very large scale is not common in this country. The farms are usually relatively small, and the herds of cows vary from ten or twelve up to one hundred or more. The milk is usually sent to a large dairy company or to a milk dealer in one of the big towns. In the smaller towns the farmer often himself delivers the milk to his customers direct. In Ireland, where the population is smaller, milk is sent to a creamery, often one run on co-operative lines, and there separated, the cream being used for butter, and the separated milk returned to the farmer as food for pigs.

Milk deteriorates very quickly when the conditions under which it is obtained are not those of extreme cleanliness. Hence the producer must exercise continual

vigilance, both during milking and in the cleaning of the vessels into which the milk is put. Apart from pathogenic bacteria, which may in certain circumstances find their way into the milk, there are always large numbers of bacteria which gain admittance. Even before the milk enters the bucket the milk has been contaminated by micro-organisms, chiefly harmless lactic acid bacteria, which were lodged in the ducts of the teats. Milk as secreted by the mammary glands is sterile. Once outside the body milk receives large numbers of bacteria from the air, from the body of the cow, and from the hands and clothing of the milker as a rule. In ordinary fresh milk the number of bacteria per cubic centimetre is never likely to be less than 10,000, and may rise to five or even ten times this amount.

It is to be regretted that no measures are taken by health authorities to test milk for cleanliness or for the bacterial content. In many cases the results would be astonishing. With simpler and more rapid methods for estimating the dirt in milk and the degree of bacterial contamination, much will probably be done in the future. The reductase test, which is based upon the decolourisation of a solution of methylene blue, seems well adapted for rapidly giving information as to the relative number of bacteria in a sample of milk. All that is needed is a saturated alcoholic solution of methylene blue, 5 c.c. of which are diluted with 195 c.c. of distilled water. The milk (10 c.c.) is mixed with 1 c.c. of this diluted methylene blue solution, covered with a little paraffin oil, and left to stand at a temperature of 45°-50° C. When decolourisation takes place at the end of an hour the milk is unfit for drinking; if the colour persists for periods between one and three hours the milk may be regarded as having a purity inversely proportional to the time required for decolourisation. A milk that retains its colour for more than three hours is satisfactory.

Given healthy animals receiving good food and pure water the wholesomeness of the milk depends largely upon the care bestowed upon the cows, and upon the dairy utensils. Another factor, of course, is the cooling of the milk immediately after milking, so that bacteria in the milk do not rapidly increase. The grooming of the cows, the brushing and washing of the udder before milking, and the provision of a separate room for milking should receive careful attention. The milker should have clean clothes and hands, and the practice of wetting the hands with milk before and during milking should be forbidden; dry milking is a very important factor. The milk should at once be strained through an efficient strainer. The newer strainers, in which the milk first passes through a fine wire sieve and then through cotton wool which can afterwards be thrown away, or a bag of closely woven material which can be thoroughly washed and steamed after each milking, are usually very satisfactory. All vessels used for the reception of milk should first be washed with cold or lukewarm water, then with boiling water, or if a supply of steam is available they may be steamed with the live steam. If such precautions as the above are taken, and the cows are healthy and have been kept under sanitary conditions, and fed with wholesome food and pure water, the milk will be found to satisfy all reasonable requirements. It will keep well, and the producer will soon find that the extra care which he has taken will be repaid by the ready sale of the milk, oftener at a higher price than milk which deposits dirt on standing, and only keeps good for a relatively short time.

Most of the milk produced is consumed as such. However, very large quantities are worked up for **butter** and **cheese**.

We discuss the manufacture of these products in the next two sections. A very considerable amount of **milk sugar** is also extracted from milk, usually from the whey which is left over after making cheese. The manufacture of milk sugar is described on page 78*a*.

BUTTER

Butter can be made from fresh or sour cream or from whole milk. Generally the cream is allowed to sour or ripen before being churned. This gives a larger yield of butter and the flavour is better. The ripening of cream is accelerated by keeping it at a fairly warm temperature, 60°-70° F., and using a starter. The starter may be a pure culture of some lactic acid bacteria, or a little sour milk or buttermilk. First pasteurising the cream and then employing a pure starter is the best means of obtaining cream of the required ripeness, and butter made under these conditions is much more uniform in character.

The composition of butter according to Storch is:—

	From Fresh Cream.	From Ripened Cream.
Water	13.03 per cent.	13.78 per cent.
Fat	83.75 ,,	82.97 ,,
Protein	0.64 ,,	0.84 ,,
Milk sugar	0.35 ,,	0.39 ,,
Mineral substances	0.14 ,,	0.16 ,,
Salt	2.09 ,,	1.86 ,,

It is thus seen that 83-84 per cent. of butter is fat and the rest is water with small quantities of protein, milk sugar, mineral matter, and 1-2 per cent. of salt which has been added in the making.

The percentage of water in butter is liable to considerable variations, and may reach as much as 20 per cent. In this country 16 per cent. is regarded as the maximum limit.

In the churning of cream the globules lose their spherical shape and collect in larger particles, which usually have a granular form. The evenness of grain of the butter after churning is of importance, and attention is paid by the maker to this point. Well ripened cream, churned at the proper temperature and not too long, gives butter of a good grain.

When the butter has been got into this granular state, it must be thoroughly washed to remove the buttermilk, which otherwise would cause the butter to rapidly become rancid. The temperature at which this is done is also of importance.

When the butter has been washed as free from buttermilk as possible, it is salted, and for this purpose a pure salt is required. It should be free from magnesium salts, otherwise it tends to become moist and then set in hard lumps, which prevents an even distribution of salt through the butter.

The manufacture of butter on a large scale is carried out in precisely the same manner as on a small scale, except that the churns and workers are run by machinery.

In America, in Germany, and to a less extent in Ireland, machines which combine a churn and a butter worker have been introduced into butter factories, so that it is now possible to work, wash, and salt the butter in the same vessel as that in which it was churned. The best known of these machines are the Astra and the Simplex. Attempts have been made to combine a separator with the churn and butter worker, and in Sweden at the present time several of these machines are in use.

Pure butter varies considerably in appearance, colour, taste, and smell, according to the breed of the cow, the food, the time of the year, and method of making. As has already been mentioned in speaking of milk, the fat which is present in the cream in an undercooled state passes into the solid condition on being made into butter. Butter is characterised by the relatively high percentage of glycerides of the lower fatty acids. Other fats contain a much smaller quantity of these glycerides so that a determination of the percentage of lower fatty acids serves as one of the

best methods for the detection of adulteration with some animal fat such as margarine. When the fatty acids are isolated from butter fat it is found that the following are present :—

Butyric acid -	$C_4H_8O_2$ (volatile)	Myristic acid	$C_{14}H_{28}O_2$ (non-volatile)
Caproic „ -	$C_6H_{12}O_2$ „	Palmitic „	$C_{16}H_{32}O_2$ „
Caprylic „ -	$C_8H_{16}O_2$ „	Stearic „	$C_{18}H_{36}O_2$ „
Capric „ -	$C_{10}H_{20}O_2$ „	Arachidic „	$C_{20}H_{40}O_2$ „
Lauric „ -	$C_{12}H_{24}O_2$ (non-volatile)	Oleic „	$C_{18}H_{34}O_2$ „

The proportions in which these acids are present in normal butter are subject to variation, but it is generally found that the glycerides of the first four make up 8-9 per cent. of the total. Almost certainly the glycerides are mixed, that is to say, the glycerin group is combined with different acid radicals, so that butter can hardly be regarded as a mixture of simple triglycerides. There is difficulty in proving this, but Partheil and Velsen, who made an artificial butter from the triglycerides of fatty acids, in the proportion in which they are present in butter, found that it had a higher solidifying point than natural butter.

The specific gravity of pure butter fat at 100° is from 0.865-0.868, the melting point varies from 28°-34.7° C., the solidifying point from 19°-23° C.

Butter fat is insoluble in water, soluble in alcohol, and very soluble in ether, chloroform, benzine, petroleum ether, etc.

The usual **analysis of butter** is confined to the estimation of the water, the fat, and the salt, and the determination in the pure butter fat of the amounts of soluble fatty acids, insoluble fatty acids, the refractive index, and the iodine value.

Water.—Samples having been taken from the bulk by means of a sampler like a cheese borer, they are put into a wide-mouthed stoppered bottle, which is then placed in warm water (40° C.). The fat, when melted, is shaken vigorously, and about 5 g. are poured into a porcelain dish containing pieces of pumice stone. The dish is then dried at 100° until the weight is constant, or very nearly so. It is not advisable to dry the butter for longer than three hours, for the continued heating tends to change its composition.

A rapid method for the estimation of water is to simply heat the butter in a dish, stirring all the time with a glass rod. When the butter ceases to froth and the casein has a brown colour, all the water has been driven off, and the dish is allowed to cool and is again weighed.

Fat.—The dried fat and pumice stone from the previous experiment is transferred to an extraction cartridge, which is then placed in a Soxhlet extractor. The dish from which the butter and pumice have been scraped is washed out well with ether, which is poured over the cartridge, and the extraction is proceeded with in the ordinary way. A layer of extracted cotton wool should be placed on the top of the cartridge to prevent fine particles of pumice stone from being carried over.

The Röse-Gottlieb method is also very useful for the estimation of the fat. Weigh out 2 g. of butter on fat-free paper, and place it in the Gottlieb tube, add warm water to make up to 10 c.c. (as for milk), then 1 c.c. of ammonia, and 10 c.c. of 95 per cent. alcohol. Shake the whole well, cool the tube and shake out with ether and petroleum ether, as in the analysis of milk.

Salt.—This can be estimated by dissolving a known weight of butter in ether, to which a little water has been added. The salt dissolves in the water, the fat in the ether, and the two can be separated with a separating funnel. The aqueous solution is then titrated with decinormal silver nitrate, neutral potassium chromate solution being used as the indicator.

Another method is to ignite the butter carefully in a small platinum dish, extract the sodium chloride from the ash with water, and titrate as above.

An examination of the butter fat is necessary to determine whether adulteration with some other fat has taken place. A pure sample of the fat is obtained by melting the butter at a temperature of 40°-50° C., and filtering it through a dry filter.

The refractive index is usually determined with a Wollny-Zeiss butter refractometer. Full details of how to use this instrument are supplied by the makers (Carl Zeiss, Jena), and it will therefore suffice to note that at 25° C. natural butter fat has a refractive index of 49.5-54.0 divisions. At 40° C. the number of divisions on the same instrument is from 40.5-44.4, and fat in exceptional cases 47.

Margarine fat has a higher refractive index—58.0-66.4 divisions at 25° C., and 48-52 divisions at 40° C., so that it is possible to detect adulteration with margarine if considerable quantities have been used. The refractive index will hardly serve to detect small quantities, for the figures obtained for genuine butter vary too much. Another substance used in considerable quantities for adulteration of butter is cocoa-nut fat, and this has a refractive index of 33.5-35.5 at 40° C.

There are several well-known chemical tests for the purity of butter fat of which the following deserve notice.

1. **The Reichert-Meissl Value** (p. 64).—Pure butter fat may have a Reichert-Meissl value as low as 20 or as high as 34, but it is seldom that genuine butter falls below 24. Margarine in which a very small quantity of these lower fatty acids is found has a Reichert-Meissl value of 1 or 2, not more as a rule.

2. **The Hehner Value** (p. 64) for genuine butter fat can vary from 85.5-91, the average value is 87.5. In margarine the value is higher.

3. **The Koettstorfer or Saponification Value** (p. 62) is very high for butter, lying between 220.5 and 332 for butter fat. This serves to detect adulteration with many fats whose saponification value is much less.

4. **The Iodine Value** (p. 63).—The iodine value of pure butter fat lies between 25.7 and 49, and it is particularly useful in detecting adulteration with cocoa-nut fat.

The above are the chief tests employed in the chemical examination of butter fat. As margarine is the most usual adulterant of butter, its peculiarities as compared with butter fat have been noticed. See *Margarine Manufacture*, pp. 85-87; also p. 64.

Colouring of Butter

Butter is nowadays usually coloured, except perhaps during a few of the summer months. The public demand is for a bright yellow butter, so that if the article fails to have the desired colour the sale is prejudiced. The materials used in the colouring of butter are generally harmless in their effect upon the consumer, and the practice is not prohibited by health authorities (see p. 87).

In this country, **Annatto**, which is got from the fruits of the *Bixa orellana* tree, is usually employed. The colouring matter after extraction is dissolved in some vegetable oil. In this condition the annatto is easily incorporated with the butter, and an even yellow colour is obtained. Too much annatto gives a reddish unnatural colour to the butter, and this should be avoided.

Saffron, curcuma, extract of marigolds, juice of carrots, are all used as butter colours. Latterly, some of the well-known yellow aniline dyes have been used for colouring butter, and whilst there is no evidence that they are injurious to health in small quantities, it would doubtless be preferable to use one of the vegetable substances previously mentioned.

Test.—A very complete scheme to be used in testing the colouring matter in butter has been drawn up by A. R. Leeds (*The Analyst*, 1887), and reference should be made to this paper if full directions for making the various tests are wanted.

Preservatives.—Certain preservative materials are used to increase the keeping properties of butter. These preservatives are as a rule similar to those used in preventing milk from turning sour. Boracic acid and its salts are the usual preservatives, and once the fat of the butter has been removed, they can be tested for in the manner already described in the section dealing with milk.

CHEESE

In its simplest form cheese may be regarded as the solid portion of milk except the milk sugar. It is true that a little milk sugar usually does get into the cheese, but the bulk is not retained. The casein, the fat, and the milk salts make up new cheese, and the nature and composition of the many different kinds of cheese indicate that much variety is possible. In milk the casein is present in a colloidal-like form and is probably a lime-casein compound or compounds. The addition of an acid or of some specific enzyme like the one in rennet causes the casein to split up into paracasein (the curd) and whey.

What changes actually during the coagulation of the casein is not well understood; although Hammersten's explanation of the splitting up of the lime-calcium compound or compounds is generally accepted, it is not easy to give proof. The souring of milk may then be regarded as a cleavage of the lime-casein compounds with the formation of curd and whey.

When rennet is used to curdle milk the curd differs considerably in physical properties from that obtained from milk which has either soured spontaneously or has been treated with an acid.

The souring of milk which takes place ordinarily when it is kept is due to lactic acid which forms as a result of the action of lactic acid bacteria upon the milk sugar. The lactic acid which thereby arises acts upon the lime-casein compounds, decomposing them and causing the precipitation of paracasein in the form of curd. The same effect is produced by the addition of a few drops of a mineral acid to milk.

Cheese is prepared to a small extent from the curd which is obtained when milk sours spontaneously, but it is never good, and cannot be got to ripen properly.

The usual way of making cheese is to allow rennet to act upon milk. The class of cheese which results depends upon the temperature at which the renneting takes place, the acidity of the milk before the rennet is added, the quantity of rennet employed, and the subsequent handling of the curd. Every well-known variety of cheese is prepared according to a definite scheme, the above-mentioned factors being altered in different cases. Rennet contains an enzyme rennin, or chymosin, which brings about the decomposition of the casein of the milk into paracasein and whey albumin. The coagulum in this case differs in chemical and physical properties from the curd which is obtained when an acid acts upon milk. The former contains lime salts, whereas the latter does not, owing to the acid having dissolved the lime. The rennet curd is also more elastic, and not sticky.

Rennet can be bought in powder or fluid form. It is extracted from the lining of the stomach of the calf, in which it is found in considerable quantities. Formerly the stomach was dried, and a piece taken whenever cheese was being made. Now the commercial powders or liquids can be bought very cheaply, and they are more satisfactory, for it is possible to determine their strength, a circumstance which is of great help in the proper making of cheese.

Rennet powder and tablets are usually very active, although the actual amount of enzyme which they contain is very small. One part of rennet powder will often coagulate 250,000 or more parts of milk. The liquids are not so strong, 1 : 10,000 being about the average strength.

In order that cheese of a regular quality may be obtained, it is usual to use a "starter" to ripen the milk before renneting. This "starter," which is similar to that used in ripening cream, is a pure culture of lactic acid, and controls the development of the micro-organisms, with the result that those which are present in the milk are prevented from developing by the activity of the lactic acid bacteria, which increase more rapidly.

To ascertain when the milk is sufficiently ripe for renneting it is usual to make a so-called rennet test, which consists in taking a measured quantity of milk (say 4 oz., or about 140 c.c.) and adding to it a diluted rennet extract (½ oz., or 5 c.c.). The mixture is then stirred and the time taken for coagulation is noted in seconds. For cheddar cheese the time is from 45-60 seconds. When the milk coagulates more slowly than this it is an indication that the milk is not sufficiently ripe.

There are so many different kinds of cheese that particulars of their manufacture would necessitate more space than is available in this article, and reference should, therefore, be made to books which deal with cheese-making from the practical side. To properly understand the chemical changes that take place in making cheese, the following is a brief description of the manufacture of **cheddar cheese**.

Great care is exercised in getting pure milk, for it is impossible to make good cheese if the milk is dirty.

The night's milk is run into a jacketed vat, the next morning the cream is skimmed off, mixed with the proper proportion of starter and then returned to the vat. The fresh morning's milk is then added and the temperature is carefully regulated to about 85° F. After standing for some time the rennet test is made and if the milk is found to be of the desired acidity, the whole of it is renneted. The amount of rennet to be added depends upon its strength, but usually 1 oz. to 20 gals. of milk is about right; this represents as a rule .04 per cent. of rennet. After the milk has been stirred it is left to coagulate, which should take place in about three-quarters of an hour. The curd must then be tested (usually this is done with the finger), and if ready, it is cut with special knives so that the curd is left in small dice-like pieces. The temperature of the vat is then gradually raised to about 102° F. and the contents stirred. This heating and stirring makes the curd firmer, so that the whey is expelled. A test is usually made to ascertain if the curd is sufficiently ripe. A small piece of curd, well pressed with the hand, is taken, placed against a hot iron and then with-

drawn. The curd draws out into threads and the length of these t
to decide whether the curd is sufficiently ripe for the purpose. The
curd.

If the ripeness is judged to be satisfactory the whey is run off, an
where it "mats" and forms a solid block, and acidity develops rap
grinding of the curd followed by salting, after which it is packed
the press. Considerable pressure (1-1½ tons) has to be used before t
but at first a pressure of ½ cwt. or less is needed. The subsequent
mould, the banding, etc., are technical operations which are empl
ripening room. In this room the cheese undergoes many changes
"ripening."

The process of **ripening** is a very important factor in cheese-mal
insipid and indigestible. During the process of ripening a large
casein is rendered soluble. The changes that take place during ripe
has it been satisfactorily explained what causes them. Without qu
take part in the process, and the lactic acid bacteria and others wh
important factors. The enzymes, *i.e.*, rennin and pepsin (both of
be reckoned with, and, according to Babcock and Russell, a specifi
by them galactose, also assists. The chemical changes which ta
interesting, although as yet they remain unexplained in some cas
alterations brought about in the casein. The casein, in fact, undergo
and instead of remaining as an elastic curd it becomes more and m
be largely converted into simpler nitrogenous compounds such a
relatively simple substances such as leucine, tyrosine, etc. There
cheese a number of decomposition products such as alanine, g
cadaverine, and ammonia.

The milk sugar present in small quantities in new cheese soon u
and the gas which is formed causes holes which are a characteristic

Soft Cheese.—In addition to the different varieties of hard
number of types of soft cheese made either from whole milk or
has been added. Some of these cheeses are eaten fresh, whil
three to six weeks.

Colouring of Cheese.—In some districts chee
highly with annatto, which is used in aqueous solutio
as in the case of butter.

Adulteration of Cheese.—The direct adulterati
be limited to the extraction of the butter fat from th
made, and the substitution of some other and cheaper
of cheese may be said to take place when some fat is
the cheese is described and sold as having been made f

Analysis of Cheese.—An average sample, taken with a che
a mortar, and (1) the **water estimated** by drying first at ord
desiccator over H_2SO_4, then at 100° for eight hours in the stea
with sand before drying. (2) **The fat** is estimated by first drying
and then extracting with ether for two hours in a Soxhlet appa
satisfactory, and Weibull (*Zeit. für Untersuchung der Nahr- und G*
(*Milch Zeitung*, 1904) have devised more rapid and accurate m
originals should be consulted.

(3) **Protein.**—In new cheese the casein has undergone little ch
considerably a good deal of it has become converted into simpler
which are soluble in water.

To distinguish between the soluble and the insoluble protein of
filtered, and the protein and basic decomposition products in the e
tungstic acid. The precipitate is collected, washed, and the nitro
method. To find out how much of this soluble nitrogen is present
a portion of the original filtered aqueous extract is distilled w
estimated by passing it into standard acid.

The total water-soluble nitrogenous compounds are determi
original filtered extract by evaporating it to dryness, and analysi
the figures obtained in this last experiment, minus the amoun
and that present as ammoniacal compounds, represent the amide n

Other means of estimating the amount of protein are also
precipitation method, but the above is complete and satisfactory.

The total nitrogenous matter, soluble and insoluble, present
determining the nitrogen present in 2·3 g. of the original substance

hreads enables the cheese-maker
longer the threads, the riper the

l the curd transferred to coolers,
dly. The next operation is the
into cheese moulds and put into
he cheese is taken from the press,
removal of the cheese from the
yed before it is removed to the
which are known collectively as

king, for a freshly-made cheese is
proportion (38 per cent.) of the
ning are not well understood nor
estion, both bacteria and enzymes
ich flourish in an acid medium are
which come from the rennet), must
enzyme found in milk, and called
ce place during ripening are very
s, but the results are seen in the
s a considerable degree of change,
ore plastic until ultimately it may
s albumoses, peptones, and even
are also present in well-ripened
latamic, acid, lysine, putrescine,

ndergoes lactic acid fermentation,
feature of some kinds of cheese.

pressed cheese there are a large
milk to which more or less cream
t others are allowed to ripen for

e is coloured more or less
, instead of dissolved in oil

on of cheese may be said to
e milk before the cheese is
fat. Indirectly adulteration
removed from the milk, and
rom whole milk.

ese borer, is rapidly ground up in
inary temperatures in a vacuum
m oven. Soft cheese is ground
with sand in a porcelain basin,
atus. The method is not very
enussmittel, 1909), and Siegfeld
thods, for details of which the

ange, but in one that has ripened
nitrogenous compounds, some of

a cheese a water extract is made,
tract are precipitated by phospho-
gen in it determined by Kjeldahl's
as basic decomposition compounds,
ith magnesia, and the ammonia

ned in a known quantity of the
ng by Kjeldahl's method. Thus
t of nitrogen present as protein
itrogenous substances.
used, *e.g.*, Ritthausen's copper

in cheese can be estimated by

Adulteration.—Adulteration of cheese is almost entirely restricted to removal of fat. With modern emulsifying machines it is possible to substitute some cheaper fat for the valuable butter fat extracted from the milk from which the cheese was made. **Margarine cheese** is a product which has been made in this way (see p. 87).

To detect this form of adulteration, the fat of the cheese is isolated, and then examined as though it were butter. A determination of the Reichert-Meissl value, the refractive index, and other tests employed in the detection of margarine in butter are used. To obtain sufficient fat for the purpose, the cheese is ground up with very dilute sulphuric acid, and the liquid afterwards whirled in the centrifuge; this serves to separate the fat, which is pipetted off and purified by melting and filtering through a dry filter paper.

Statistics.—The quantities of **butter** and **cheese** imported into the United Kingdom are :—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Butter - - -	4,300,000	4,300,000	£24,500,000
Cheese - - -	2,600,000	2,500,000	6,800,000

Against this there were in 1910 *exported* 9,000 cwt. butter (*value* £56,000) and 8,000 cwt. cheese (*value* £38,000).

The corresponding figures for the United States are :—

IMPORTED IN 1910.

Butter and butter substitutes - - -	1,360,000 lbs. (value, $298,000.
Cheese and cheese substitutes - - -	40,817,000 lbs. (value, $7,053,000).
Cream - - -	732,000 galls. (value, 578,000.

EXPORTED IN 1910.

Butter and butter substitutes - - -	3,140,000 lbs. (value, $785,000.
Cheese and cheese substitutes - - -	2,846,000 lbs. (,, $441,000.

THE MANUFACTURE OF MILK SUGAR

By Geoffrey Martin, Ph.D., M.Sc., B.Sc.

LITERATURE

G. Zirn.—*Milch Zeitung*, 1895, 481, 497. The processes here described are still in use.

When milk is used for making cheese (see p.) or casein (p.), the w… left can be used for the manufacture of **milk sugar.** The solid matter in wh… Milk sugar, 4.6-5.0 per cent.; protein (chiefly albumin), 1.0; fat, 0.3; mine… When whey is boiled the albumen coagulates, and if the boiling is continued … impure variety of milk sugar is obtained. This crude milk sugar, which is … Switzerland, and there known as "Schottensick," contains 85 per cent. of milk … of water, and nearly 5 per cent. of mineral matter, along with small amount… When large quantities of whey are obtained, as in cheese or casein factories, t… whey is carried out in *vacuum pans.*

The whey must be worked as quickly as possible, otherwise fermentation … sugar being partially decomposed into lactic acid, which then inverts the mil… thereby occasioning a serious loss. The addition of a little sodium carbona… neutralise most of the acid—care being taken to allow the liquid to remain ver… to prevent loss of milk sugar by inversion. The addition of *formalin* (100 … of whey) also acts well, but is somewhat expensive.

Sour milk must be carefully neutralised before concentrating.

The evaporation takes place at 60°-70° C. in vacuum pans (best in double-eff… economise steam), the evaporation taking place in such a way that as the wa… whey is allowed to flow in continually at such a rate as to maintain the level of … The liquid thus gradually concentrates to 30°-32° Bé., when it contains 60 per c… it is then run out into iron crystallising tanks of 700 l. capacity and allowed t… the cooling must be hastened by surrounding the tank with cold water or by imm… in it. The temperature must fall from 60° C. to 20° C. in twenty-four hours. A … mass of crude milk sugar crystals separates at this stage. The mass is centrifuged … as is employed in beet sugar manufacture, pp. 162-163). 100 parts of whey yie… *crude yellow sugar*, which contains 88 per cent. milk sugar, 12 per cent. water …

There passes away from the centrifugal machines about one-third of the or… still containing much milk sugar, which is often extracted by passing in live s… density 15° Bé.; this coagulates the albumen, which collects on the surface, an… as a cake when the syrup is run off; the cake is pressed between cloth, ground … poor material, *e.g.*, potatoes, turnips, etc., and used as a food for pigs.

The syrup at 35° Bé. (warm), thus freed from albumen, is once more ran… concentrated, allowed to crystallise (after standing some days in well-coole… water, and centrifuged, when a further yield of 0.3-0.7 per cent. of crude … Total yield of crude milk sugar is about 4.35 per cent.

The liquid from this second crop of milk sugar is used as a manure, … albumin and non-crystallisable sugars, but it cannot be used for feeding pigs … It has been worked for lactic acid and calcium phosphate.

Another way to obtain the crude milk sugar is to neutralise, or nearly s… with sodium or ammonium carbonate, then boil, when the coagulated albu… along with the fat, in the form of a porous scum. This is skimmed off and … evaporated in a vacuum pan.

Purification of the Milk Sugar.—The crude yellow milk sug… described, is sometimes dried and sold as such. More often it is sent to … into pure *white* milk sugar. The crude milk sugar is dissolved at 50° C. … headed copper boiler. The solution contains 24-27 per cent. milk sug… charcoal and 2 per cent. of acetic acid is added (to precipitate albume… nearly to the boiling point, some magnesium sulphate is added (to precipita… the liquid is boiled for some minutes. The liquid foams. The tempera… sediment collects at the bottom. The liquid is pumped upwards (by a … copper vessel covered with wood, and then allowed to flow downwards th…

The precipitate is rich in P. and N. and is a valuable manure. The … tint, is concentrated in vacuum apparatus to 35° Bé (65 per cent. sugar … by adding a little fat and increasing the pressure.

Finally the concentrated liquid is run into iron crystallising vessels, … milk sugar is centrifuged. The mother liquors are worked for further … sugar thus obtained is further refined by dissolving in water (to 15° Bé), h… sulphate is added, the liquid is filter pressed, concentrated to 32° Bé, … crystallising vessels, centrifuged, and the resulting white sugar is dried in … in a stream of hot air, cooled, ground, and packed for export.

Milk sugar is sometimes adulterated with other sugars and sometimes with mineral substances. The former are detected by the change in the rotatory power, particularly in what is termed the birotation ratio, which is the initial rotation, that obtained immediately after the solution is made, divided by the rotation at the end of twenty-four hours. The increase in weight of the ash above the normal (0.035-0.05) denotes mineral adulteration.

Milk sugar, although expensive, is often used in brewing, as it is not fermentable by ordinary yeast, and so remains in the finished product as unchanged carbohydrate, thereby increasing the "extract" of the beer. Also sold as a constituent for children's food.

VI.—INDUSTRIAL CASEIN

By G. Martin, Ph.D., M.Sc.

LITERATURE

L. Myddelton Nash.—Art. "Casein" in *Thorpe's Dict. Chem.* (1912).
R. Scherer.—"Casein." London, 1906.
Geoffrey Martin.—"Industrial Casein," *Chemical World*, 1912, I. 353.

The chemical nature of casein, as well as its use in the production of cheese, has been discussed in the preceding article.

Manufacture.—The machine-separated milk used for casein manufacture, containing 3 per cent. casein, 0.4 per cent. milk albumen, 0.15 per cent. fat, 4.7 per cent. sugar, 0.7 per cent. minerals, must be as *fat-free* as possible. Milk rich in colostrum (taken from cows soon after calving) is unsuitable, as it yields soft curds which squeeze through filter cloths and hold much water. Milk containing coagulated albumen (*i.e.*, boiled or highly heated milk) also yields a curd difficult to work.

Industrial casein is usually precipitated by gradually running in the proper amount of *dilute sulphuric acid*, with constant stirring, into the milk until it becomes clear yellow with separation of the *curd*, which is drained, washed with cold H_2O, pressed (or centrifuged), broken up and dried — best in a Passburg vacuum drier, but also on trays in hot air drying chambers or cylinders. Great care must be taken not to heat too strongly or the casein dries to a dark colour. The dry casein is ground and packed for export.

However, the curd may also be precipitated by *HCl*, *phosphoric acid*, *lactic acid*, *acetic* or *citric acid*, by *rennet*, by *self-souring*, and by electrolysing milk at 120° F. with N or C electrodes. In order to render the curd *fat-free and white*, the precipitated curd, after well washing and pressing, is sometimes stirred to a pulp with water (100 curd to 50 water), and then steamed for twenty-five to thirty minutes in a wooden vat with about 150 parts of a 1 per cent. solution of soda. This is to remove lactic acid and butter fat. After heating, the mass forms a thin milky fluid, which is transferred to a separate vessel to cool, and is then precipitated with dilute HNO_3. The precipitated casein collects at the bottom, the supernatant liquor is run off, and the casein rinsed with water, settled, and water decanted, the washings being repeated until the wash-waters are neutral. The casein is then drained on filter cloths, pressed, and dried on trays in drying chambers at 120°-140° F. One hundred parts of curd yield 45 parts purified casein, free from lactic acid and butter fat.

Among other methods proposed for preparing industrial casein, the following may be mentioned:—

1. The curd is precipitated from the skimmed milk with dilute H_2SO_4, the yellowish product redissolved in alkali (sod. bicarbonate), and reprecipitated with dilute acetic acid (German Patent, 135,350).
2. The casein is precipitated by leading SO_2 gas into milk warmed at 50°-70° C. The process is complete in a few minutes, the time taken being so short that there is no danger of inversion occurring (German Patent, 184,300).
3. A fat-free casein is obtained by mixing decreamed milk with alkali, warming, removing the fat by centrifuging, and then precipitating casein in the ordinary way with acid (German Patent, 135,745).

Uses.—Industrial casein is used (1) as a painting material; (2) as a mucilage and cement; (3) in the preparation of plastic masses, forming substitutes for horn, celluloid, ivory, etc., and especially for "galalith"; (4) as a dressing and colour-fixing medium in the paper and textile industries; (6) as a food stuff; (7) for "fining" wine. This is cheaper and better than albumen. See p. 245.

Statistics.—In 1910 England imported casein of value £54,000. The export reached £21,000. The United States in 1910 imported 3,769,000 lbs. of casein of value $304,000. The chief firm in England is *Casein, Ltd.*

Casein Glue (see **Glue**, p. 596). — Casein can be converted into an excellent glue by stirring it up with 400 per cent. distilled water and 3½ per cent.

sod. bicarbonate, standing for five to six hours, and adding an antiseptic to prevent mould. Sometimes shellac is added. The glue is now ready for use. Such glues can be applied cold.

Very often the casein is dissolved in borax, soda, or ammonia. The applied casein glue is made insoluble by formaldehyde. A *waterproof* glue is obtained by dissolving casein in lime.

In the woodworking trades casein glues threaten to displace ordinary gelatine glues because casein glues can be applied cold (so that all the trouble of melting the glue is avoided), can be made waterproof, and by their use certain delicate effects are attainable in veneering work which are impossible with gelatine glue, since the latter must be applied *hot*, and is not waterproof.

Casein as a Sizing Material.—Casein is widely used for sizing paper and similar materials (see **Paper**).

It is dissolved in alkaline solutions, and mixed into the paper pulp. The process is especially useful when the paper pulp has to be moulded or pressed into relief forms; as the casein size is very resistant to heat or moisture. Extremely beautiful art papers are sized with casein, and some photographic papers are also casein sized, the papers being extremely resistant to heat and moisture, and thus keep well in the tropics. The leather and textile industries also employ casein for "dressing" and "finishing" purposes. The great advantage of casein over gelatine is that it is entirely precipitated by the subsequent addition of alum, whereas most of the gelatine is lost in the back water. In the printing of materials a casein product containing silicic acid is used instead of egg-albumen; it is prepared by dissolving the casein by heating with dilute NH_3, adding sodium or potassium silicate, and adding phosphoric or acetic acid until the whole, which first solidifies, again becomes fluid (German Patent, 161,842).

Casein Water Paints.—See under **Paints**, p. 512.

Manufacture of Bone Substitutes from Casein.—Casein when mixed with formaldehyde gives an insoluble horn-like product, which is used as a bone, horn, and celluloid substitute. See under **Celluloid** substitutes and **Galalith**, p. 210.

Casein Food Stuffs (see **Cheese, Milk Powders,** and **Guttmann's Nutrient Milk Flour**) consist of casein mixed with carbohydrates, such as gluten-free oatmeal, and a small quantity of aromatic substances.

Visem is a more recent similar food, containing lecithin and salts of glycero-phosphoric acid. **Sanatogen** is said to consist of 95 per cent. casein and 5 per cent. of sodium glycero-phosphate. White powder, soluble in H_2O, fat-free; lactose-free (see German Patents, 98,177, 1898; 99,092, 1897; 99,093, 1897; 99,094, 1897; 152,380, 1903; 152,450, 1903; 118,656, 1899. See also *Chem. Ztg.*, 1899, 371; 1900, 538, 718). **Eulactol** is a white powder prepared by evaporating milk *in vacuo* at 98° F.; it contains 33.25 per cent. albumen, 46.3 per cent. fat, 14.3 per cent. of carbohydrates, and 4.3 per cent. saline matter (see D.R. Patent, 98,441; *Chem. Ztg.*, 1899, 851).

Plasmon (casein) is an albuminoid preparation from milk, occurring as a yellowish white powder containing 75-80 per cent. albumin, 5-7 per cent. Na_2CO_3, 5-10 per cent. fat and milk sugar—very assimilable (see German Patent, 100,977, 1898. *Chem. Ztg.*, 1900, 538, 718. *Chem. Centralblatt*, 1899, II., 533, 1130; 1900, I., 677, 828).

Dr Riegel's Milk Albumen is said to contain 85 per cent. albumin, 8.2 per cent. water, 0.31 per cent. fat, 7.4 per cent. mineral matter. The curd is precipitated from the milk by ethyl sulphuric acid.

Eucasein is a casein ammonium compound, soluble in water (see *Chem. Ztg.*, 1899, 851; D.R. Patent, 84,682, 1895; 108,053, 1897).

Nutrose is a *sodium caseinate* (see German Patents, 85,057, 1894, and 89,142).

For **Sanose** see *Chem. Ztg.*, 1898, 686; 1899, 371; *Chem. Centralblatt*, 1899, I., 1294.

For **Casein** foods, separated from milk by citric acid and containing calcium phosphates, see German Patents, 115,958; 123,622, 1898; 137,000, 1901; 122,458, 1899.

Vi-Casein, a soluble sodium caseinate, contains 76-78 per cent. proteins, is free from milk sugar (nearly), and so is used for diabetic patients.

Acknowledgment.—The author's best thanks are due to *Mr L. Myddelton Nash* for much valuable advice on this subject.

VII.—CONDENSED MILK AND MILK POWDERS

By W. H. Stephens, A.R.C.S.

The prime feature which characterises the operation of reducing milk to a smaller volume is the necessity for minimising changes due to the action of heat, both on the various constituents of the milk and on their distribution in the product. As regards the former, the most important, unless the heating is unduly prolonged, are the coagulation of the albumen which occurs at about 70° C., the modification and resulting change in the colour and in the solubility of the casein,

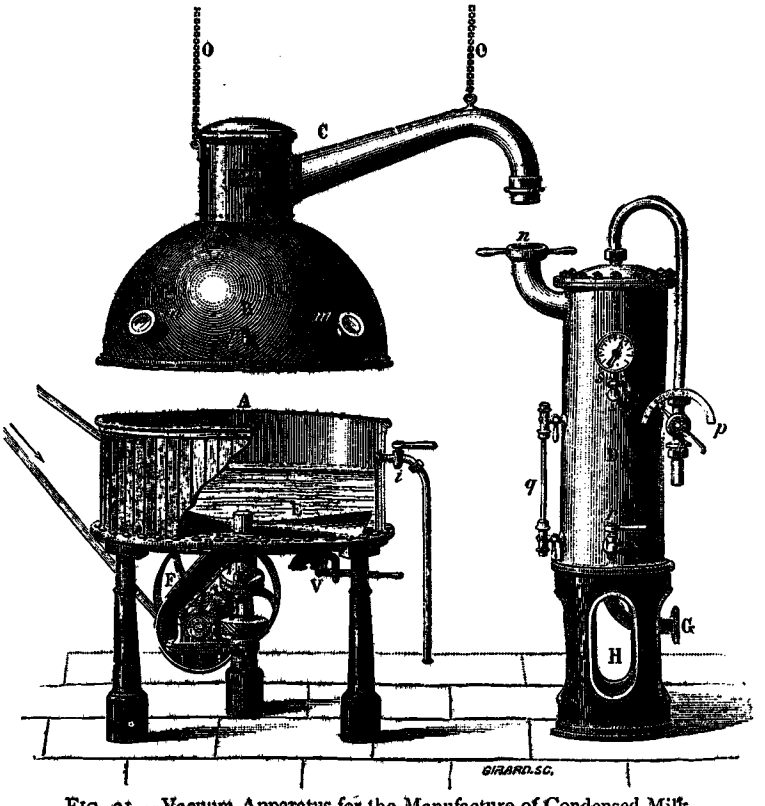

Fig. 21.—Vacuum Apparatus for the Manufacture of Condensed Milk. (Egrot, Paris.)

and the caramelisation of the milk sugar. Of the second class of changes, the separation of the fat, and the formation of large crystals of milk sugar are most to be feared.

Many of these transformations may be obviated either by arranging that the milk shall never be subjected to high temperatures, or by conducting the operation in such a manner that the milk is treated at a high temperature for a very short period of time.

The separation of the fat is due primarily to the increased tendency of the minute fat globules to run together when an emulsion, such as milk, is heated,

One method of meeting this difficulty consists in reducing the size of the fat globules before the commencement of the operation. This process is known as "homogenisation," and consists in breaking up the globules by violent disruptive treatment, ordinarily effected by driving the milk under high pressure through minute orifices, or by forcing it at a high velocity against stationary surfaces.

Alkaline bodies, such as bicarbonate of soda, are commonly added mainly to reduce the acidity of the milk and thus prevent rancidity, and also to obviate the loss of volatile fatty acids. These substances also act as emulsifying agents, and minimise the separation of the fat.

The presence of crystals of milk sugar in condensed milk gives a gritty taste to the product, and can only be avoided by carefully watching the concentration.

Condensed Milk.—In condensing milk it is usual to concentrate the milk in bulk in a vacuum pan at a temperature of about 40°-50° C. Concentration at a low temperature has also been effected by using an air blast to aid in the evaporation of the water. Cane sugar is usually added, but unsweetened milks are also brought on to the market. The concentration may be carried much further when sugar has been added, the product consequently having better keeping qualities. Sweetened milks generally contain about 25 per cent. of water; unsweetened milks about twice as much.

The following table* gives the composition of some of the milks:—

	Condensed Whole Milk.			Condensed Skim Milk.
	With Cane Sugar.	Without Cane Sugar..		
		Condensed Half Bulk.	Condensed Third Bulk.	Condensed to Quarter Bulk.
Water	27.88	76.70	66.91	27.43
Fat	9.62	6.80	9.75	0.29
Protein	10.27	5.89	8.95	11.59
Milk sugar	14.20	9.13	12.50	13.60
Cane sugar	36.06	...	...	44.92
Ash	1.97	1.48	1.89	2.17
	100.00	100.00	100.40	100.00
Sp. gr. at 15° C.	1.29	...	1.0945	...

Milk Powder.—All attempts to dry milk by processes such as those used in condensing milk, and involving the treatment of the milk in bulk for a considerable period of time, have resulted in a product of very inferior quality. In the processes now in use the milk is treated in the form of films or spray for a relatively short time.

The film apparatus in common use comprises a rotating cylinder, on which a thin layer of milk is evaporated to dryness in the course of a single revolution. In Ekenberg's process the temperature is low and the operation is effected *in vacuo*. Kunick † also uses a low temperature, but facilitates the evaporation by means of a current of air. The Just-Hatmaker ‡ process is probably the most interesting and successful of this type. A temperature in excess of 100° C. is maintained on the surface of the cylinder, and the milk is in consequence reduced to dryness so rapidly that injurious changes are inhibited. The time during which the milk is exposed on the surface of the cylinder is never more than $2\frac{1}{2}$ seconds, and may be as low as $\frac{1}{2}$ second.

The apparatus used is known as a "twin-cylinder" drying machine, and is shown in Fig. 22. It is composed of two cylinders *a*, placed side by side and slightly separated from each other. The milk is fed continuously to a trough *b*,

* From Kirchner's "Milchwirtschaft," p. 599 (5th edition, 1907).
† English Pats., 5,189, 1906; 1,692, 1907.
‡ Eng. Pats., 21,617, 1902; 8,743, 1903.

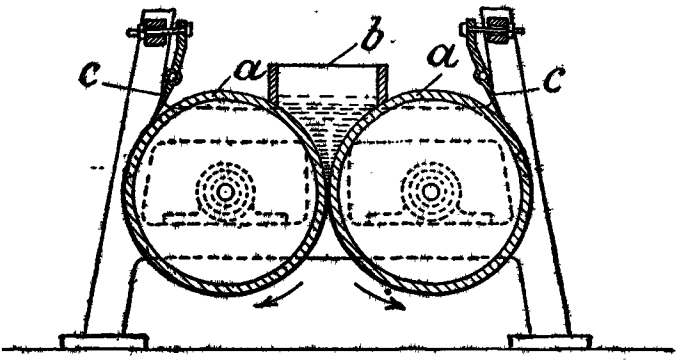

FIG. 22.—Twin Cylinder Drying Machine for Milk Powders.

constituted by the upper parts of the cylinders and suitable end walls, is carried round as a film on the surfaces of the cylinders, and is removed in the dry state by scraper *c*. The cylinders are heated internally by means of steam of 40 lbs. pressure. In consequence of the temperature used, this process has the additional advantage of providing a sterile product.

The spray evaporators are constructed in the form of chambers, to which are admitted a fine spray of milk in close proximity to a current of warm air. The spray is almost instantly transformed to a dry powder, and is carried by the air current to depositing or filtering chambers. In some cases the spraying devices are so constructed as to homogenise the milk. In a recent process of Ekenberg's,* carbonic acid gas is used as a drying agent in order to impart keeping qualities to the product. It need scarcely be said that in all processes where air is used, it should be previously washed and filtered and, preferably, sterilised.

Milk powders as a rule contain from 4-7 per cent. of moisture, a proportion of this being combined with the milk sugar as water of crystallisation.

The following table † gives the composition of some of these milk powders, along with that of the milk from which they were produced :—

	I. Whole Milk.	II. Resulting Powder.	III. Theory.	IV. Skim Milk.	V. Resulting Powder.	VI. Theory.
Water	87.8	5.16	5.00	91.95	3.55	5.00
Fat	3.4	26.22	26.48	0.15	2.55	1.59
Proteid	3.4	25.47	26.48	3.49	35.45	36.09
Milk sugar	4.7	33.93	36.59	4.70	45.60	49.89
Cane sugar	...	1.20	...	...	2.80	...
Ash	0.7	6.22	5.45	0.70	7.89	7.43
Total	100.00	98.20	100.00	100.00	97.84	100.00

Columns III. and VI. are calculated on the supposition that no loss of cream or fat occurs on drying the milk. The close agreement of the numbers so obtained (columns III. and VI.) with those actually found by analysis of the dried powder (columns II. and V.) show that practically no loss of cream, fat, or protein occurs in the condensing process.

* Eng. Pat., 16,375, 1909.
† Kirchner, "Milchwirtschaft," 5th edition, p. 603.

Statistics.—The following figures show the value of the English import and export :—

IMPORT.

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Condensed milk, sweetened	...	942,900	£1,640,000
,, unsweetened	...	66,700	113,000
Milk powder, not sweetened	10,600	20,400	36,800
Nestlé's milk food	2,300	1,700	13,700

EXPORT.

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Condensed milk, sweetened	310,000	423,000	£886,000
,, unsweetened	14,000	16,000	38,000
Milk powder	24	285	1,076

The United States in 1910 *exported* 13,311,000 lbs. of condensed milk (value, $1,023,000).

Analysis.—The methods adopted are as a rule those applied to ordinary milk, condensed milk being diluted for analysis, milk powders being as a rule examined in the dry state.

The only method of special interest is that for the estimation of milk and cane sugars. The proteins are first precipitated, and a portion of the milk boiled with Fehling's solution. A further portion is then inverted with hydrochloric acid, and the product also boiled with Fehling's solution.

Approximate methods, depending on the altered relationship of sugar to easily determined constituents, *e.g.*, ash, are used for manufacturing purposes.

VIII.—MARGARINE MANUFACTURE

By G. Martin, Ph.D., M.Sc.

LITERATURE

Most of the facts in the accompanying article were supplied privately by firms interested in the manufacture of margarine. Much of the published literature is very poor, and often describes methods in vogue over twenty years ago and now abandoned.

G. Hefter.—"Technologie der Fette u. Öle," vol. iii. Berlin, 1910. Gives the best account.

Lewkowitsch.—"Oils, Fats, and Waxes," vol. iii. (1901 edition).

Dr K. Windisch.—"Margarinekäse." Berlin, 1898.

"Die Margarine-Fabrikation," von Th. Büddinger. Separat-Abdruck aus dem Organ für den Oel- und Fetthandel. 2nd Edition. "Verlag. N. Besselich." Pp. 16. Trier, 1910.

ARTIFICIAL BUTTER, MARGARINE

Butter fat is a mixture of the glycerides (both simple triglycerides and mixed glycerides) of acetic, butyric, caproic, caprylic, lauric, myristic, palmitic, stearic, arachidic, and oleic acids. It also contains small amounts of cholesterol and natural colouring matters (lactochromes). The average proportions of the acids are as follows: Stearic acid, 0.49 per cent.; palmitic acid, 18.23 per cent.; myristic acid, 11.08 per cent.; lauric acid, 16.4 per cent.; oleic acid, 36.1 per cent.; caproic, caprylic, and capric acids, 3.23 per cent.; butyric acid, 6.13 per cent.; glycerol, 12.5 per cent. Cow butter consists of fat, 83-91 per cent.; water, 7.5-13.75 per cent.; casein, 0.5 per cent.; milk sugar, 0.3 per cent.; ash, 0.3 per cent.; salt, 1-2 per cent.

Since glycerides of the same fatty acids are present in varying amounts in many other fats and fatty oils, the problem which confronts the margarine manufacturer is the blending together of these fats so as to produce a substance having the same chemical composition as butter. Chemically this could be done by separating pure glycerides from the various fats (making them artificially if necessary) and then blending them together in the exact proportions in which they occur in butter fat. On the large scale this operation is quite impracticable on account of cost, so that the art of the margarine manufacturer consists in utilising the fats ready to hand, and blending them together in such proportions as most closely simulates the natural product. This has been so successfully achieved that many of the margarines now on the market resemble butter so closely in physical and chemical properties that the analyst has often very great difficulty in deciding whether a sample consists of true or artificial butter. There can be little doubt that ultimately a margarine will be produced having almost exactly the same constituents as natural butter, and therefore indistinguishable from it either by chemical tests or natural flavour.

Manufacture of Margarine

The following ingredients are used in various percentages according to the quality of the margarine it is desired to produce: oleo oil, neutral lard, cocoa-nut oil, earth-nut oil, sesamé oil, and cotton-seed oil. The refining of oils has become so perfect of late, through the application of the so-called American "Wesson Process," that the oils used are now absolutely flavourless and neutral. About 50 per cent. of carefully soured cream or milk is churned through the above-named fats, and these, being quite tasteless, adopt the milky and buttery flavour of the soured cream. To the highest grades up to 10 per cent. of pure butter fat (the

highest percentage allowed by law) is still added, which brings the quality so near the real article that even experts often cannot detect any difference.

All countries nowadays make about the same blends. Generally speaking, one can say that higher grades contain about 10 per cent. of oil, 70 per cent. of oleo oil, and 20 per cent. of cocoa-nut oil, whilst lower grades contain up to half oil and half animal fats.

Process of Manufacture.—The milk, after a searching bacteriological and qualitative examination, is passed through the separators where the cream is separated from the milk. The cream is either churned into butter, or, what is usually more profitable, sold as cream. The separated milk is at once pasteurised (*i.e.*, heated to a temperature a little below its boiling point in order to destroy bacteria) and immediately cooled to nearly freezing point, remaining at this temperature until required for the "souring tanks," when it is again warmed to a moderate temperature suitable for the souring culture which is then added. The souring culture is prepared in the bacteriological laboratory in the most careful manner, since the buttery flavour of the whole yield of margarine is dependent upon this. The milk is then allowed to "ripen" in a series of great open tanks, in which the milk is gently worked to and fro during the process; the floor is of concrete, and clean water is kept flowing over it, while the walls of the room are of glazed white ware, so that at this stage the danger of introducing foreign bacteria is minimised.

The milk thus prepared is now mixed in suitable quantities with the above-mentioned animal and vegetable oils in suitable proportions, and the mixture is thoroughly churned for not more than one hour in a suitable machine. The temperatures vary from 20°-45° C. The higher the quality the lower the churning temperature, the object being to retain as much as possible of the delicate milk flavour, which a high temperature largely destroys. In this way the product gets the characteristic smell and taste of butter.

Then, the property of butter to brown and froth being due to casein and milk-sugar, suitable proportions of these, or sometimes also of "Elaine," extracted from yoke of eggs, are added to high grade margarines.

In the churning machines the ingredients are thoroughly beaten into an emulsion or cream, the mixture being pulverised into single globules such as butter fat forms in milk, the process being regulated if necessary by means of steam or ice water sent through the steam jacket with which the churn is provided. The mass is then run out into large wooden tanks (sometimes coated with marble slabs, cleanliness being everywhere of the utmost importance). While running out in a thin stream from the churns the fluid margarine is met by a high-pressure jet of cold water, which pulverises the margarine, so that the disintegrated globules after solidifying resemble butter granules very closely.

This method of chilling the margarine has always been a source of dissatisfaction to the manufacturer, as it is impossible to perfectly control it, and even under the most favourable circumstances it did not give the best results for the following reasons:—

1. The milk serum in the emulsion is partly replaced by water.
2. Part of the souring culture is washed out, this resulting in an irregular and insufficient development of the souring ferment during the subsequent operations.
3. The chilling not being carried out at a sufficiently low temperature, the finished margarine is always of a softer and more greasy texture than butter.

To remedy these defects a process has recently been patented by Mr E. Schou which does away with the water cooling. The emulsion as it leaves the churn is spread out into very thin layers of about one-fiftieth of an inch in thickness on two large drums, revolving at the same speed but in opposite directions. These drums are cooled down by means of refrigerated brine to a temperature of about −10° C., so that the very thin layers of emulsion immediately crystallise on the drums, and *while retaining the whole of the milk serum*, are scraped off in thin flakes, and treated as subsequently described. The advantages of this method are very great, viz.:—

1. The whole of the milk serum and souring culture being retained, a perfect control of the flavour of the margarine is secured.
2. Through the more effective cooling, the texture of the margarine becomes firm and at the same time pliable, and both to the naked eye and under the microscope it is hardly to be distinguished from butter.

The process has been worked for some time by one of the largest firms of margarine manufacturers in this country with such success that the best qualities of margarine thus prepared are equal, if not superior, to the best qualities of pure butter.

The solidified margarine is now removed in wooden waggons to the fermenting rooms, where the excess of water is allowed to drain off, and the souring culture in the milk allowed to develop and flavour the whole mass of margarine. After "ripening" for a sufficient time, the mass is transferred to large kneading machines in order to squeeze out the excess of water and obtain a homogeneous mass. Salt may here be kneaded in to taste, together with colouring matter to produce the fine yellow colour characteristic of butter. Many colouring substances are sold (some even being aniline dyes).

Two harmless **colouring mixtures** much used are these:—

(*a*) Orlean, 80 parts; curcuma root (turmeric), 80; olive oil, 240 by weight; saffron, 1 part mixed with alcohol, 5 parts by weight. Macerate the orlean and turmeric with olive oil, express, make up the weight of the filtered liquid to 240 parts by weight with olive oil; then add the filtered saffron-alcohol extract, stir, and expel the alcohol by heating the mixture.

(*b*) Moisten 30 parts of finely powdered alum with 3 parts of turmeric extract, spread out and dry the powder in a warm place; then pulverise finely, and store, protecting the product from the light. A pinch of the powder added to a churnful of milk or cream before the churning imparts a beautiful golden colour. The turmeric extract is made by adding 1 part powdered turmeric to 5 parts alcohol, and macerating together for about a week; then filtering. After the kneading the margarine is moulded into lumps, pats, etc., ready for the market.

As a food margarine is little (if at all) inferior to butter, and being prepared from the freshest and purest materials, is usually cleaner than butter as prepared in the dairy.

Distinctive Tests between Butter and Margarine (see also pp. 64, 75).—1. The Reichert-Meissl value (see under Fat Analysis) for butter is very large (20·33 cm.). That of most fats range from 0.5-1.5 cm. (cocoa oil, 7·8). Margarine makers now often add glycerides of volatile acids, so as to obtain the same number as with true butter.

2. The saponification value of butter is high (221·233), that of other fats low. The addition of cocoa-nut oil to the margarine raises its saponification value to that of butter.

3. The refractive index of butter is 1.4590-1.4620 at 25° C. (butyro-refractometer scales, 49.5-54). That of margarine is 1.4650-1.4700 (58.6-66.4 butyro-refractometer divisions). Cocoa-nut oil lowers the refractive index of margarine to that of butter.

4. True butter fat contains less than 1 per cent. of stearic acid. Most margarines contain 10-20 per cent., and even more. For other tests see under Butter.

S. H. Blichfeldt (*Jour. Soc. Chem. Industry*, 15th July 1910, p. 792, vol. xxix.) has devised a process for the estimation of **butter** and **cocoa-nut fat** in margarine.

The fat is saponified by a mixture of aqueous potash and glycerol, and the fatty acids are liberated by acidification with sulphuric acid. The resulting mixture is distilled in a specially designed apparatus, made by Becker, London.

The distillate is treated with an excess of decinormal soda solution and transferred to a 200 c.c. measuring flask. The total volatile acids are determined by titrating back with decinormal sulphuric acid. The neutral soap solution is now treated with excess of decinormal silver nitrate solution, and 10 per cent. of solid sodium nitrate is dissolved in the liquid in order to salt out all the sparingly soluble silver salts. After making up to 200 c.c., the precipitated silver salts are filtered off, and the excess of silver nitrate is determined volumetrically in the filtrate. The volatile fatty acids are thus determined as soluble and insoluble silver salts.

The ratios of soluble to insoluble silver salts, derived from butter and cocoa-nut fats respectively, differ considerably from one another, and afford a ready means of determining these substances in presence of one another.

Suet substitutes consist of a mixture of suet (tallow) and cotton-seed oil or cotton-seed stearin.

Lard substitutes are mixtures of lard or "lard stearine" (p. 26), with cotton-seed stearine, maize oil, cocoa-nut oil, and other similar oils. In Germany such substitutes are heated with onions and condiments, and sold as cooking fat (*bratenfett*).

Margarine Cheese is made from milk from which the cream has been removed, and to which margarine fat has been added. Otherwise the operation is just like cheese-making in the ordinary way (see under Cheese). In 1910 about 1,600 cwt. (value, £2,500) were imported into Great Britain.

Statistics.—The amount of **margarine** imported into the United Kingdom is given by the following figures:—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Margarine - - - -	1,101,900	1,120,800	£2,900,000
,, cheese - -	1,200	1,600	2,500
Imitation lard - - -	231,000	275,000	600,000

Exported was 7,000 cwt. (value £17,000), in 1910, of **margarine**; and 2,700 cwt. (value £6,600) of imitation lard.

The United States in 1910 exported 74,556,000 lbs. of lard substitutes (value, $6,887,000), and 3,418,000 lbs. of oleo-margarine or imitation butter (value, $350,000).

The author thanks Mr Paul Arup for much information regarding the modern raw materials used in the manufacture of margarine.

IX.—MANUFACTURE OF FATTY ACIDS AND CANDLES, INCLUDING HYDROGENATION OF FATS

By G. Martin, Ph.D., M.Sc.

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Candles are commonly composed of free fatty acids such as stearic and palmitic acids. Hydrocarbons such as paraffin wax or ceresin are now very largely used, either alone or (more usually) mixed with fatty acids. Certain waxes, such as beeswax, carnaüba wax, spermaceti, etc., are employed in making some of the more expensive sorts of candles, while ordinary tallow enters into the composition of some of the inferior qualities.

Obviously good candle material must burn without smoke or smell, must not soften and bend under usual conditions of temperature, and when melted, must form a fluid which can be readily drawn up by the wick. Tallow is soft and burns with a foul smoky flame, and so is only used for the cheaper kinds of candles. Some of these objections apply to inferior sorts of paraffin.

Preparation of Fatty Acids for Candle-Making (also for Soap makers).—The fats are saponified by several processes:—

Saponification by Lime (de Milly's Process).—Some 6,500-7,500 lbs. of fat are placed in a copper digester and 1-3 per cent. of lime (or magnesia) and a little water is added.* Saturated high-pressure steam is then turned on, and the whole is heated for six to eight hours with steam at a pressure of 8-10 atmospheres. Under these circumstances a temperature of over 176° C. prevails within the digester, and the fat is almost completely hydrolysed into glycerol and fatty acids as follows:—

$$\underset{\text{Tristearin, 890 parts.}}{C_3H_5(O.CO.C_{17}H_{35})_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Glycerol, 92 parts.}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid, 852 parts.}}{3C_{17}H_{35}COOH}$$

At the same time the lime present is turned into an insoluble calcium salt, thus:—

$$\underset{\text{Tristearin.}}{2C_3H_5(O.CO.C_{17}H_{35})_3} + \underset{\text{Lime.}}{3Ca(OH)_2} = \underset{\text{Glycerin}}{2C_3H_5(OH)_3} + \underset{\text{Calcium stearate (insol. lime soap).}}{3(C_{17}H_{35}.CO.O)_2Ca}$$

A modern digester consists of a copper boiler (iron discolours the fatty acids) 5-6 ft. in diameter and 18-30 ft. high (Fig. 23). The contents are agitated either by paddles or rotating spiral screws.

* Superheated water alone at a temperature of over 200° C. (15-20 atmospheres pressure) is capable of almost completely hydrolysing fats. The presence of lime, however, allows the temperature and pressure required for saponification to be greatly reduced.

The glycerol collects in the water underneath the oily layer of fatty acids. From time to time a sample of fat is withdrawn and analysed, and when the process of saponification is thus found complete enough, the mass is allowed to stand until the separation into two layers—fatty acids above and glycerin ("sweet") water below—is complete. The two layers are then pumped off into separate vessels.

The fatty layer is now boiled up with steam, and sufficient sulphuric acid added to decompose the lime soap contained in the fatty acids, thus :—

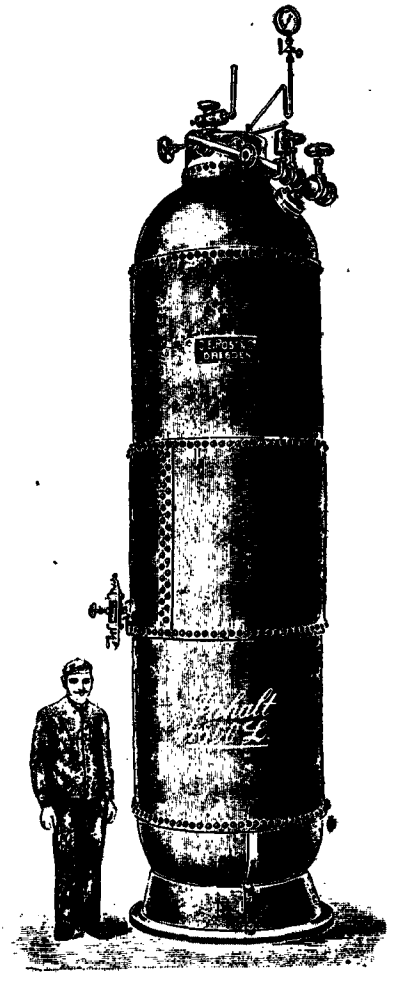


FIG. 23.—Copper Digester for the Manufacture of Fatty Acids by de Milly's Process. (Rost & Co., Dresden.)

$$(C_{17}H_{35}CO.O)_2Ca + H_2SO_4 = CaSO_4 + 2C_{17}H_{35}COOH$$

Calcium stearate. Sulphuric acid. Calcium sulphate. Stearic acid.

On standing, the calcium sulphate separates as a sludge at the bottom of the watery layer, while the fatty acid forms an oily layer above : the two layers are separated.

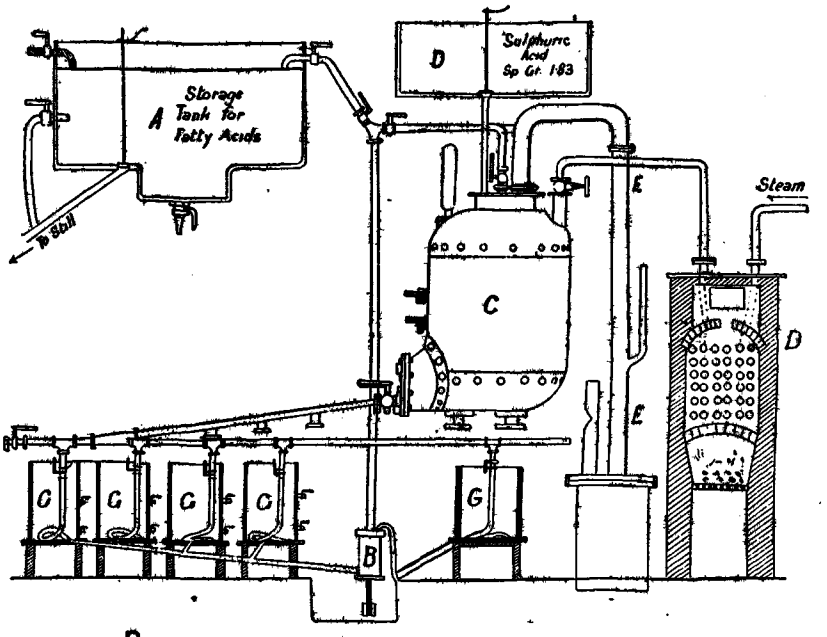
The further treatment of the fatty acids depends upon the quality of the fat used for saponification.

If the best tallow or fatty oils have been employed, the fatty acids thus obtained may be white enough for direct pressing and conversion into candles as described below, while the glycerin water may be worked up for good quality glycerol as described under Glycerol.

Usually, however, the best sorts of tallow are used for edible purposes, and the candle or soap maker works with inferior dark-coloured fats, which yield fatty acids too dark for direct use in candle-making. Consequently, the fatty acids so obtained are either distilled with steam, as described below, or else the neutral fats are treated with concentrated sulphuric acid (acid saponification) in a manner we will now describe.

Saponification of Fats by Means of Sulphuric Acid.—This process is usually used for inferior fats obtained from garbage, putrid bones, etc. The fatty acids from the lime saponification process (from which the glycerin has already been extracted) are often subjected to this process in order to slightly increase the yield of candle material, since the sulphuric acid turns the fluid oleic acid into oxystearic acid, a hard white solid capable of being utilised in candle-making; thus, while the lime saponification process alone yields 45-47 per cent. of solid fatty acids, the acid saponification process yields 55-63 per cent., with a slightly lower melting point.

The process is carried out as follows (Fig. 24): The dark coloured fat is melted in an iron tank by means of a closed steam coil, and heated until most of the water present is expelled. Next, the melted fat is forced by means of the pump B into a copper boiler C, and 3-6 per cent. of concentrated sulphuric



PLANT FOR ACID PROCESS OF FAT SAPONIFICATION

FIG. 24.

acid of sp. gr. 1.83 run in from the lead-lined tank D. The whole is heated for five to six hours at 130° C. by means of a closed copper coil, through which superheated steam from the superheater D is passed. The sulphurous fumes arising from the action of the acid on the fat are pumped away through EE by means of a water jet contained in the vertical pipe, which discharges into F. A complicated action ensues; the hot, strong acid attacks the fat, thus:—

$$\underset{\text{Tristearin.}}{C_3H_5(O.CO.C_{17}H_{35})_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Stearic acid.}}{3C_{17}H_{35}COOH} + \underset{\text{Glyceryl sulphate.}}{C_3H_5\begin{matrix}(OH)_2\\O.SO_2OH.\end{matrix}}$$

The hot water at the high temperature employed also saponifies the fat into glycerol and free fatty acid, so that instead of the theoretical 11 per cent. sulphuric acid required according to the above equation, in practice only some 3-4 per cent. are necessary. The fats blacken considerably owing to the destruction of tissues and membranes present by the concentrated sulphuric acid. At the temperatures employed the fatty acids themselves are scarcely affected. If, however, the temperature is allowed to rise too much, the sulphuric acid finally attacks them, converting them into sulphonic acids. Some of the glycerol is destroyed. Part of the oleic acid present is converted into an unstable sulphonic acid, thus: *—

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}COOH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphonated stearic acid.}}{C_{17}H_{34}\begin{matrix}COOH\\O.SO_2OH\end{matrix}}$$

* According to Lewkowitsch (*Journ. Soc. Chem. Ind.*, 1897, 392) sulpho-hydroxystearic acid is formed.

The subsequent boiling with water decomposes this sulphonic acid into oxystearic acid, thus:—

$$C_{17}H_{34}\begin{matrix}COOH\\O.SO_2OH\end{matrix} + H_2O = C_{17}H_{34}\begin{matrix}COOH\\OH\end{matrix} + H_2SO_4$$

Oxystearic acid.

And this, in the subsequent distillation of the fatty acids, is partially converted into a solid isomeride of oleic acid, called iso-oleic acid, $C_{17}H_{33}COOH$, M.P. 44° C. There are also formed at the same time lactones and hydrocarbons of unknown constitution. The net result of the operation is an increase in the amount of solid matter capable of being used for candle material.

The action being completed, the tarry matter at the bottom of the boiler is run off, and the fatty acids boiled with water in a series of lead-lined tanks (G, G, G), the heating being effected by open steam coils contained in them. Finally, the fatty acids, now washed free from sulphuric acid, are pumped up into the storage tank A, from whence they are run into the steam still for a final purification by distillation, as described below (p. 93).

Formerly no attempts were made to recover the glycerol, and statements are even now published in standard works stating that the glycerol is almost completely destroyed. Glycerol, however, is too valuable a product to throw away, and it is now extracted with little loss from the acid and aqueous liquors run off from the fatty acids (see under Glycerol).

Twitchell's Process of Saponification.*—When concentrated sulphuric acid is allowed to act on a mixture of benzene and oleic acid at a temperature below 30° C., the following action takes place:—

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulpho-benzene-stearic acid.}}{C_6H_4(HSO_3)(C_{18}H_{33}O_2)} + \underset{\text{Water.}}{H_2O.}$$

The sulpho-benzene-stearic acid may be separated by washing the viscous oil thus produced with water. In place of benzene we may employ naphthalene or phenol

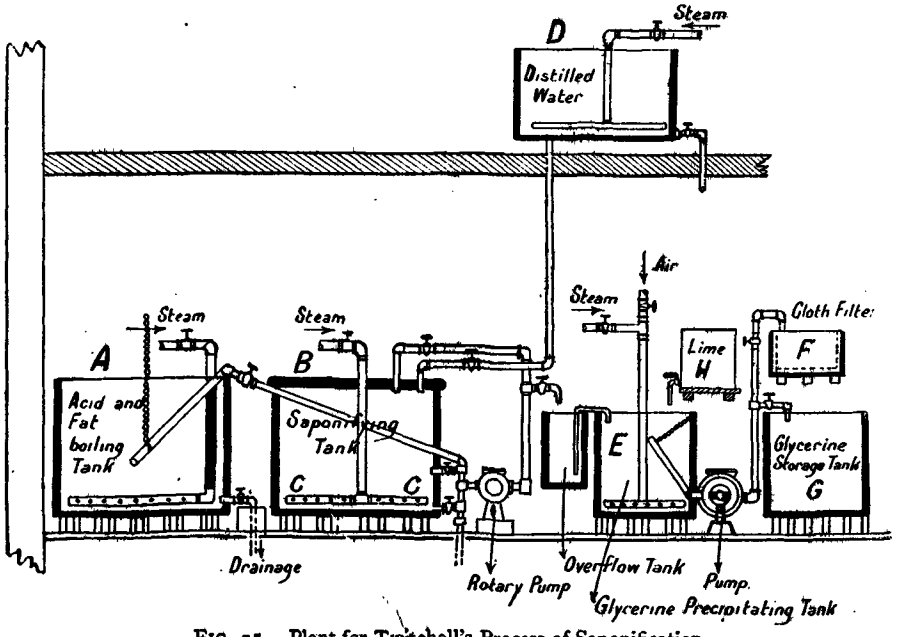


FIG. 25.—Plant for Twitchell's Process of Saponification.

* Eng. Pat., 4,741, 1898.

and obtain similar compounds, naphthalene yielding, for example, sulpho-naphthalene-stearic acid, $C_{10}H_6(HSO_3)C_{18}H_{35}O_2$.

This new series of fatty-aromatic acids has the remarkable property of readily hydrolysing fats into glycerol and fatty acids when boiled with them. The fat, previously purified by boiling with dilute sulphuric acid in a lead-lined wooden tank A, is pumped into a lead-lined wooden tank B, provided with a closely fitting cover, about one third of its weight of distilled water from D is run in, and 0.5-1 per cent. of the sulpho-benzene-stearic acid (or similar body) added. Live steam is then driven through the liquid by means of the open coil C, and the boiling continued for twelve to twenty-four hours, when the saponification will be complete. During the boiling no air must be allowed to come into contact with the fat or a dark coloured product will result; hence the lid of the saponifying tank must fit practically air-tight. Finally, the mixture is allowed to settle; the fatty acids separate out as a clear oily layer above, and the glycerol water below. The glycerol water is drawn off into E, and the fatty layer boiled up again with some fresh water for another twelve to twenty-four hours, when all the glycerol is extracted. At this stage a little barium carbonate mixed with water (1 part barium carbonate to 2,000 lbs. of stock) is added to B in order to neutralise acid in the fat, and the boiling with steam resumed until the fat is neutral to methyl orange. Finally, the mass is allowed to settle, and the glycerol water drawn off first, and then the fatty acids, which are now ready for use.

The glycerol water in E—amounting to about 60 per cent. of the volume of fat—is neutralised by a little milk of lime contained in H, the sediment allowed to settle, and the clear glycerol water pumped into G, passing if not quite clear through the cloth filter in F. From G the glycerol may be passed to the evaporators to be boiled down and distilled.

Advantages of the New Process.—1. The great simplicity of apparatus and operations.

2. The glycerol water drawn off from the fat is very rich in glycerol, yielding when boiled down a very pure product at little cost.

The **Disadvantage** is the tendency to produce dark coloured products. An apparent improvement on Twitchell's original reagent, both in respect to the lighter colour of the fatty acids produced and the smaller amount necessary for saponification is the **Dartring** saponifier (English patent 749, 1912; German patent, August 1911, V. 9847), placed on the market by the Vereinigte Chemische Werke, A.G., Charlottenburg, and Geo. Haller & Co., of London.

Other Processes of Saponification.—Colloidal metals (*e.g.*, platinum) readily hydrolise fats (see *Journ. Soc. Chem. Industry*, 1909, 611). The process promises to develop into a technically important one.

Enzymes contained in many seeds also readily and spontaneously hydrolise fats at ordinary temperatures into free fatty acids and glycerol. For further information see *Journ. Chem. Industry*, 1906 (25), p. 994; (Fokin); 1905 (24), 977 (E. Hoyer); 1904 (23), 327 (Nicloux). Nicloux states that the enzyme contained in 10 kilos of crushed castor seed which has been extracted with castor oil is able to decompose 1,000 kilos of fats and oils in twenty-four hours at ordinary temperatures. The fats are stated to yield excellent light coloured soaps.

Barbé and Garelli (English Patent, 12,210, 1907) saponify fats with ammonia under pressure, thereby producing ammonia soaps and glycerol. The ammonia soaps are decomposed by steam, the ammonia being boiled off, condensed and used again. The free fatty acids float on the surface of the glycerol water, and may be separated by decantation. Since the ammonium salts of oleic acid are first decomposed it is possible, by stopping the boiling with steam at the right point, to first separate the oleic acid, and then, by continuing the boiling, to separate the stearic and other acids.

In the patent No. 9,758, 1908, they saponify with 0.5 per cent. of ammonia (which acts catalytically in the process) with steam at 130°-160° C. under 3-6 atmospheres for eight hours, and immediately separate the resulting very pure glycerol waters of 6°-7° Be. See also Patents 24,836 and 24,837, 1908.

Distillation of the Fatty Acids.—A typical still used for this purpose is shown in Fig. 26. The melted fatty acids are run from the storage tank M into the large copper still A, which is usually heated by direct fire to a temperature of about 260° C., while steam which has been heated to 260°-360° C., in the superheater B is blown through C, C, into the mass of hot fatty acids. The fatty acids distil over into a series of copper condensers D, D, D, the liquid acids running from them down into copper coils E cooled by water in the wooden boxes K, K, K; from these coils they are drawn off, according to quality, into separate tanks. F is an auxiliary condensing arrangement, situated out of doors, for condensing the lighter portions

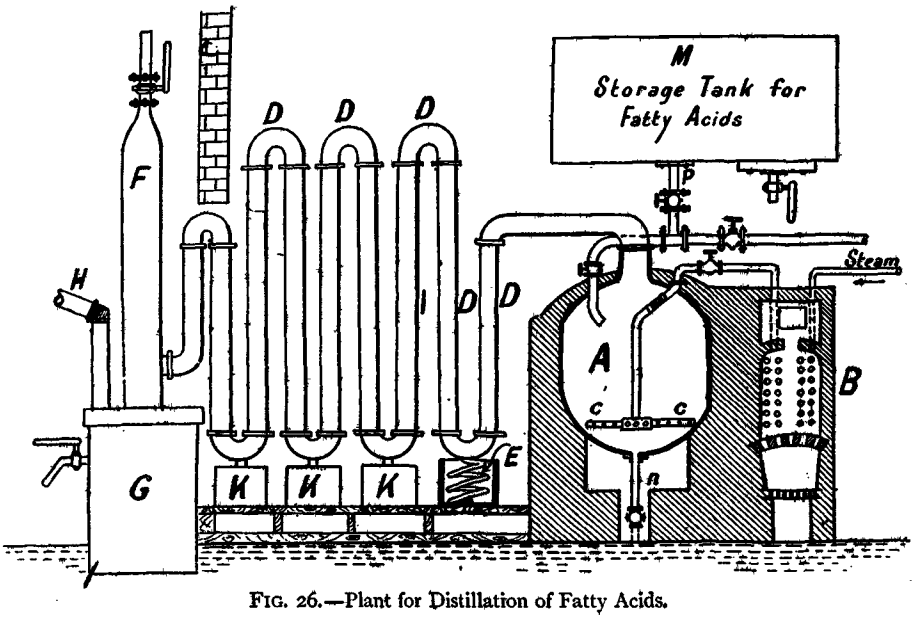


FIG. 26.—Plant for Distillation of Fatty Acids.

of the redistilled tar. A water aspirator contained in F carries the fumes into the tank G; uncondensed vapours pass off through H, and are suitably disposed of.

About 18,000 lbs. of fat may be distilled continuously, the volume in the still being kept constant by the continual introduction of fat from the storage tank M in proportion as the volume in the still decreases during the distillation.

Palmitic acid first distils over, then stearic and oleic acid, and finally lactones and hydrocarbons. The first distillate (80-95 per cent. of the whole) is white in colour, and may be pressed at once for conversion into candle material. The later fractions, which are rich in bodies produced by the decomposition of the fatty acids —such as lactones and hydrocarbons—are returned to the storage tank M and redistilled. The black residue (liquid when hot, solid when cold) which finally remains in the still is known as **candle pitch**, and is run off through the outlet pipe *n*; it is used for making insulating material for electrical machines, for waterproof paper, as a lubricant, and as a constituent of black paints; it forms about 2 per cent. of the charge.

The United States in 1910 imported 4,263,000 lbs. of candle pitch (value, $70,000), of which 1,170,000 lbs. came from the United Kingdom.

Process of Pressing the Fatty Acids.—The fatty acids, purified as described above, are now run into a series of shallow tinned iron trays arranged one above the other in racks in a cooling room, which is artificially maintained at such a temperature that the fatty acids crystallise only very slowly during ten to twelve hours, so that the crystals of stearic and palmitic acid formed are large, and thus allow the liquid oleic acid, retained between them and forming the mother liquid out of which they crystallise, to be easily expelled by pressure.

The cakes of fatty acid thus obtained are wrapped in cloth and subjected to a hydraulic pressure of 250 atmospheres in the cold. Then they are pressed at a temperature of 60° C. in a "hot press," *i.e.*, one steam jacketed so as to allow the pressing to take place at this temperature. The white hard cakes thus obtained are remelted and clarified, when they are ready for use.

The expressed oleic acid, commonly called "**red oil**," is usually cooled, when a

further separation of solid stearic and palmitic acid takes place. This is separated, and the mother liquid, consisting of impure oleic acid, is used as a wool oil or as a stock for textile soap.

Melting Points of the Fatty Acids.—These are important for their commercial valuation :—

	M.P.		M.P.
Oleic	4° C.	Elaidic	51° C.*
Oxystearic	84°-86° C.	Stearic	69° C.
Iso-oleic	44°-45° C.	Palmitic	62° C.

Process of Candle Moulding.—Candles consist of cylinders of wax or fatty acids surrounding a wick lying true in the centre in order to avoid unequal burning. These **wicks** are made of cotton threads loosely plaited together and soaked in a solution of boric acid, potassium nitrate or chloride, and ammonium chloride, sulphate, or phosphate. The plaiting causes the wick to curve when burning, and thus they burn away at the ends without causing the flame to smoke. The chemical solution vitrifies the ash of the wick, and the minute glassy particles dropping off from the bent wick leave the end free for the melted fat to ascend to the point where combustion is taking place. In the absence of this chemical treatment the wick burns off short in the flame and causes persistent guttering. Stearine or paraffin candles are moulded in special machines.

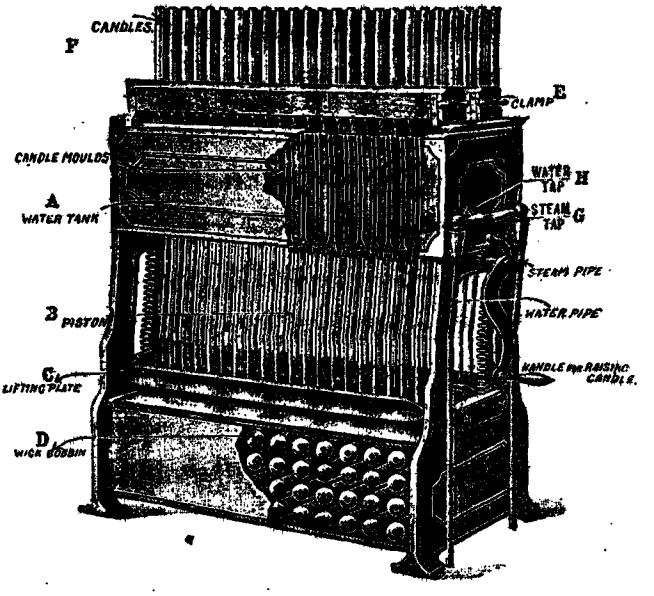


FIG. 27.—Modern Candle Moulding Machine.
(From J. Calderwood's "Manufacture of Candles," p. 15).

Fig. 27 represents an ordinary candle machine capable of moulding ninety-six candles simultaneously. It consists of a battery of moulds contained in an iron tank A, through which warm or cold water can be passed as desired in order to heat or cool the moulds. Each mould (the construction of which is shown in Fig. 28) is made of polished tin, sometimes backed by iron, and traversed by a piston which can be raised or lowered so as to force the candle out of the mould. The wicks are wound upon the bobbins D (Fig. 27), and pass up the piston rods B accurately through the centres of the candle moulds as shown in Fig. 28, and end in the candles from the previous "round," which are held in exact position in a special clamp. To use the machine hot water is first driven through the box containing the moulds so as to heat them to a suitable temperature; next the melted wax is poured into the trough, and not only completely fills the moulds, but leaves a sufficient surplus in the troughs to allow for contraction of material on cooling. Next the hot water is replaced by a stream of cold, which rapidly chills the moulds, and

* Lewkowitsch gives 44.5° C. as the correct M.P.

the candles solidify. The wicks of the candles held in the clamp above the trough are now cut, and the previous round of candles carried away for packing. The excess of candle material in the trough is now removed by means of a suitable tool, the emptied clamp replaced over the trough, and then, by operating the handle, the pistons B are pushed up the moulds, thus forcing out the candles into the holder

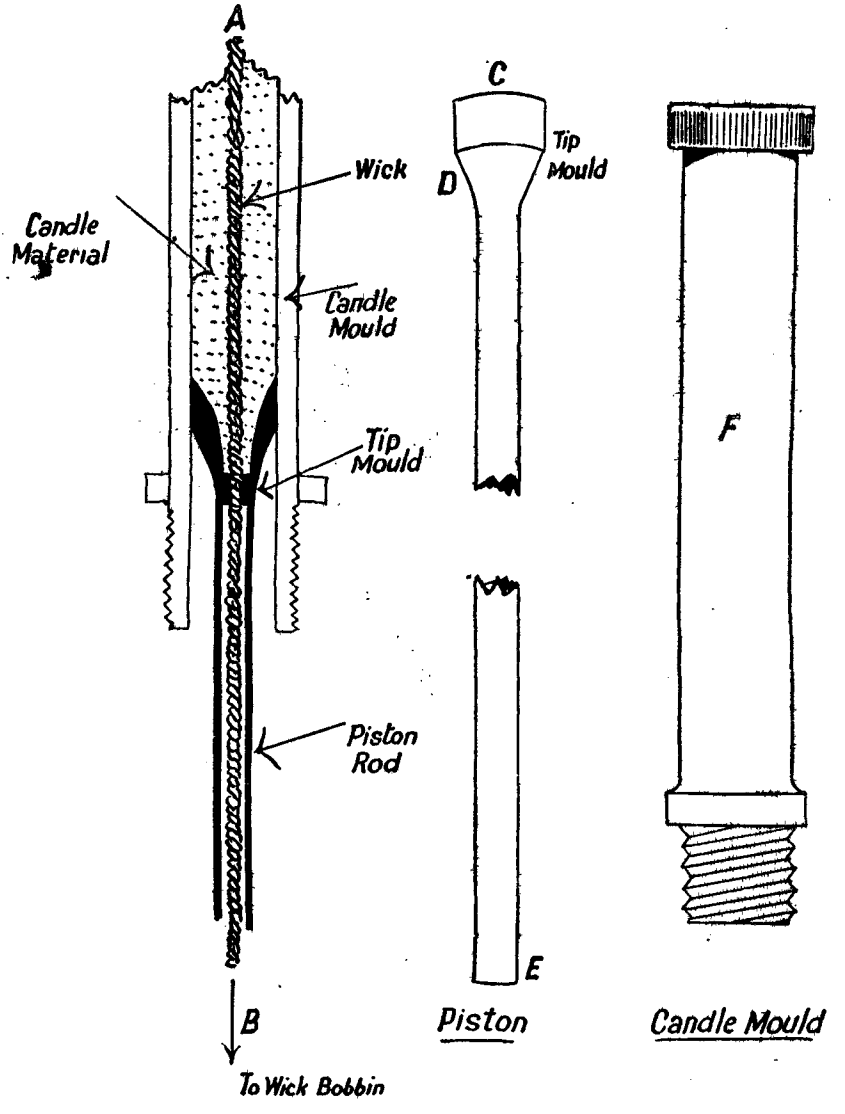


FIG. 28.—Section of Candle Moulds.

or clamp E. The wicks are drawn up with the candles, so that, immediately after the withdrawal of the first lot of candles, the pistons are lowered and another charge of wax poured into the moulds. When the surplus material in the trough is sufficiently solid, the wicks above are cut by a special knife or scissors, and the clamps containing the candles are then lifted away, and the candles ejected into a rack or

other convenient place. After the clamps have been replaced upon the machine the operation is continued until, ultimately, the bobbins D, which contain sufficient wick for several hundreds of candles, are emptied, when they are either rewound, or replaced by others.

A great advance on these machines is represented by Cowles' "Multiple" candle-moulding machines, which enormously increase the output and effect a very great economy of labour, water, steam, and floor space; thus while by the use of a small candle machine such as that just described ninety-six candles can be produced at one operation, by the use of a multiple machine of the same size no less than 360 candles can be produced by one operation. The "Multiple" machine is capable of producing no less than 518 candles at one filling, filling three times an hour, and producing per week of fifty-five working hours no less than 90,000 candles. It is fitted with patent swing-over clamps for holding the ejected candles, depositing them in a V-shaped tray attached to the clamps.

"**Self-fitting**" **candles** have conical fluted ends by which they may be fitted into any candlestick without scraping or paper. Being tapered at both ends they cannot be produced in a single mould.

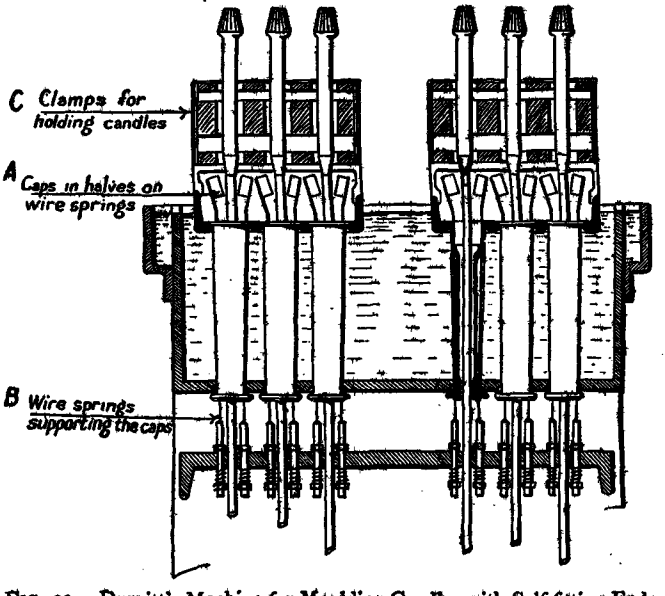


FIG. 29.—Durpitt's Machine for Moulding Candles with Self-fitting Ends.
(By the Courtesy of Price's Patent Candle Co.)

The arrangement used by Price's Patent Candle Company, and patented by their Mr Durpitt, is shown in the figure. The cap A, which forms a fluted conical butt, is in halves, each supported on wire springs B, which pass down recesses in the mould. When the candle is forced out of the mould these halved caps also rise a little, and springing apart they allow the enlarged butts of the candles to pass through; these are received in clamps C, and held in position over the centres of the moulds until the next lot of candles has solidified round the wicks, as in the ordinary "plain end" machines.

In some forms the conical ends are made by means of a movable top bed, fitted with moulds for these butts.

Usually a little paraffin is added to the stearine in order to render the wax less brittle. Also to paraffin candles varying amounts of stearine are added for similar reasons. Since low melting candle material is much cheaper than high melting material, candles are now manufactured with a thin exterior of any suitable high melting material, the interior being composed of the cheaper low melting material. Special machinery is required to perform the moulding, but the candles thus produced have the advantage of being very economical to manufacture, and not liable to gutter in burning, or cake together in packing, while the exteriors can be lettered for advertising purposes, or made of any desired colours, such colours not interfering with the combustion of the candle. **Wax** and **ceresin** candles are not moulded, because the wax at the moment of moulding shrinks away from the mould; also they stick to the form. Thick **altar candles** are made simply by

pouring molten wax down a wick hanging vertically, and then rolling between boards. Smaller candles of the same material are made by drawing the wicks repeatedly through melted wax until of the proper size. By mixing beeswax with varying proportions of paraffin and stearic acid it is possible to mould it like ordinary candles.

Colouring Candles.—The candle material is usually coloured, before moulding, with organic colouring matter, the best sorts being those soluble in alcohol, since they affect least the burning power of the candle. The stearine is melted at 65° C., and the dye stirred in. The quantity varies between 0.05 and 0.01 per cent. of the weight of candle material. Mineral colouring matters cause the candles to burn badly, while many aniline dyes fade rapidly when in contact with the stearic acid. Good results are obtained with the following dyes: *Red*—sudam IV., flexin, rose bengal, rhodamin. *Yellow*—chinolin yellow, auramin. *Green*—acid green, Victoria green. *Blue*—indulin, Victoria blue, methyl violet.

Transparent Candles for ornamental purposes may be made in a variety of ways. (1) If 100 parts of paraffin wax be melted at 80°-90° C. with 2 parts of beta-naphthol, a material is obtained which remains transparent on moulding. (2) Paraffin wax, 70, stearine, 15, and petroleum, 15, melted together, give a low melting-point transparent candle material. (3) Paraffin wax, 90, stearine, 5, and petroleum, 5, give a higher melting-point material somewhat less transparent than (2).

Statistics.—The value of candles imported into the United Kingdom in 1910 was 5,600 cwt. (value, £14,500; exported were 292,000 cwt. (value £485,200).
The United States in the same year imported 160,000 lbs., value $26,000, and exported 3,215,000 lbs., value $244,000.

Manufacture of Candle Material from Waste Oleic Acid.—Oleic acid, expressed from the stearic and palmitic acid used in candle-making, is a viscid fluid quite useless as a candle material. Many attempts have been made to turn it into candle material, but only the first process described has met with any measure of commercial success.*

1. **The Conversion of Oleic Acid into Hydroxystearic Acid.**—Oleic acid is dissolved in distilled petroleum (60° Bé.), and cold concentrated sulphuric acid† run in, the temperature not being allowed to increase beyond 40° C. The following reaction takes place:

$$C_{17}H_{33}COOH + H_2SO_4 = C_{17}H_{34}\begin{matrix}COOH\\O.SO_2OH\end{matrix}$$

Oleic acid. Sulphuric acid. Sulphostearic acid.

$$C_{17}H_{33}COOH + H_2SO_4 = C_{17}H_{34}\begin{matrix}CO\\|\\O\end{matrix} + H_2SO_4$$

Oleic acid. Sulphuric acid. Stearolactone. Sulphuric acid.

Next, live steam is blown in, whereby the sulphostearic acid is decomposed, thus:—

$$C_{17}H_{34}\begin{matrix}COOH\\O.SO_2OH\end{matrix} + H_2O = C_{17}H_{34}\begin{matrix}COOH\\OH\end{matrix} + H_2SO_4$$

Sulphostearic acid. Water. Hydroxystearic acid. Sulphuric acid.

The steam-heated mass is allowed to stand, and the water and sulphuric acid, sinking to the bottom, are drawn off. The remaining mass is extracted with hot petroleum naphtha,‡ which dissolves out the hydroxystearic acid. On cooling.

* See "The Conversion of Oleic Acid into Candle Material," by Dr Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1908, p. 489. See also p. 100*a*.

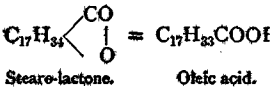
† Zinc chloride has been also used for the purpose.

‡ U.S. Letters Patent, No. 772,129—N. M. Burton, patentee; Standard Oil Company, assignee—11th October 1904.

the petroleum the hydroxystearic acid separates out as a white mass, which is filtered, dried, and pressed.

Fifty per cent. of oleic acid is thus converted into hydroxystearic acid, two modifications of which exist—the alpha variety, melting at 77°-85° C., and the beta variety, melting at 81°-85° C.

The filtrate consists of stearo-lactone and unchanged oleic acid; when it is distilled the unchanged oleic acid passes over, and part of the stearo-lactone is converted into oleic acid or iso-oleic acid, thus :—



Stearo-lactone. Oleic acid.

The recovered oleic acid is again treated with sulphuric acid as above described, and a further quantity converted into hydroxystearic acid. It is claimed that by this process no less than 85-90 parts by weight of hydroxystearic acid are obtainable from 100 parts of oleic acid.

Hydroxystearic acid used alone is not a good candle-making material, although its melting point is high; but a mixture of 3 parts of the substance with 1 part of commercial stearic acid is used for stiffening paraffin wax candles.

For recent methods of converting oleic acid into hydroxystearic acid by treating with sulphuric acid, the reader may consult the following English patents :—

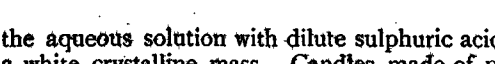
2,989, 1910.—**Dubovitz** treats benzine bone fat (1,465 kilos) with water (600 kilos) and MgO (8 kilos) in autoclave for eight hours; blows out, separates fatty acids and Mg soap from the glycerol water; dries fatty acids and Mg soap (1,412 kilos) and treats with 26 kilos of 92 per cent. H_2SO_4 for one hour; boils with H_2O. The iodine number was lowered from 44.9 to 33.2, giving 12.9 per cent. of solidified oleic acid.

10,466, 1904; 10,466A, 1904; and 19,988, 1905.—**Dreymann** treats the oleic acid with H_2SO_4, then esterifies the separated acids with methyl alcohol, and separates the pure acids by distilling *in vacuo* their methyl esters (which boil at a lower temperature than the fatty acids themselves), and decomposing them again into methyl alcohol and fatty acid by superheated steam.

24,836 and 24,837, 1908.—**Barbé, Garelli, and Paoli** treat the oleic acid with concentrated H_2SO_4, and convert the resulting anhydrides and lactones into acids by saponifying with ammonia (English Patents, 12,210, 1907; 9,758, 1908), decomposing the resulting ammonia soaps with cold water. The ammonium oleates are more soluble in cold water than the ammonium stearates, and consequently are drawn off in solution from underneath the stearic acid and stearic soaps, and a separation is thus effected of the oleic and stearic acids, the ammonia soaps being finally decomposed by boiling water, the ammonia recovered and used again, and the free fatty acid drawn off. They claim to obtain from oleic acid about 65 per cent. stearic acid melting at 70° C. (see also pp. 93, 109).

393, 1902.—**Sandberg** treats train oil with H_2SO_4 and nitrous acid. The nitrous acid converts the liquid oleic into solid elaidic acid, $C_{18}H_{34}O_2$.

2. **Conversion of Oleic Acid into Palmitic Acid.**—When oleic acid is fused with caustic alkali it is converted into palmitic acid, thus :—



Oleic acid. Caustic soda. Potassium palmitate. Potassium acetate. Hydrogen gas.

On acidifying the aqueous solution with dilute sulphuric acid, the palmitic acid is precipitated as a white crystalline mass. Candles made of palmitic acid manufactured by this method have actually appeared on the market, but the process was not commercially successful, the evolution of hydrogen making the manufacture dangerous, while the candles themselves possessed an unpleasant smell and greasy touch.

3. **Conversion of Oleic Acid into Stearic Acid.**—Oleic acid is an unsaturated acid, only differing from stearic acid by the absence of two hydrogen

atoms. Several processes have been proposed for making oleic acid take up these two hydrogen atoms and become stearic acid according to the equation :—

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}COOH} + \underset{\substack{\text{Hydrogen}\\\text{gas.}}}{H_2} = \underset{\text{Stearic acid.}}{C_{17}H_{35}COOH}$$

The processes are described in the next article on the **Hydrogenation of Fats.**

Acknowledgments.—The author's best thanks are due to Messrs Price's Patent Candle Company for much information regarding a subject which they, more than any other firm, have improved and developed. Also to Mr W. H. Stephens for much information regarding recent processes.

THE HARDENING OF FATS. HYDROGENATION OF FATS

By Geoffrey Martin, PhD.

LITERATURE

Sabatier and Senderen.—*Ann. Chim. Phys.*, 1905, [8], 4, 319; 1909, [8], 16, 70.
P. Sabatier.—*Ber.*, 1911, 44, 1984; "La Catalyse" (Paris, 1912).
A. Crossley.—*Pharm. Journ. and Pharmacist*, 1914, 92, pp. 604, 637, 676.
C. Ellis.—*Journ. Soc. Chem. Ind.*, 1912, 31, 1155.
Offerdahl.—*Ber. Deutsch. Pharm. Ges.*, 1913, 23, 558.
T. W. A. Shaw.—*Journ. Soc. Chem. Ind.*, 1914, 33, 771.

The following important patents should also be consulted :—

English Patents, 1,515, 1903; 2,520 and 13,042, 1907; 9,112, 1908; 7,726, 3,752, 26,612, and 30,282, 1910; 5,188, 13,519, 15,439, 25,326, and 15,440, 1911; 4,702, 5,773, 18,282, 18,310, 18,996, 18,998, 22,092, 23,377, 23,643, 24,084, 28,754, 1912; 10,204 and 16,283, 1913.

German Patents.—211,669, 1909; 221,890, 1910; 236,488, 1911; 260,885, and 256,500, 1913.

French Patents.—450,703, 1912; 458,445, 1913.

U.S.A. Patents. — 1,004,034, 1911; 1,004,035, 1911; 1,040,531, 1,040,532, and 1,043,580, 1912; 1,059,720, 1,058,738, 1,060,673, 1913.

Oleic acid is an unsaturated acid only differing from stearic acid by the absence of two hydrogen atoms. Several processes have been proposed for making **Oleic Acid** take up these two hydrogen atoms and become stearic acid, according to the equation :—

$$\underset{\text{Oleic Acid.}}{C_{17}H_{33}COOH} + \underset{\substack{\text{Hydrogen}\\ \text{Gas.}}}{H_2} = \underset{\text{Stearic Acid.}}{C_{17}H_{35}COOH}$$

Thus fuming hydriodic acid reduces oleic acid to stearic acid; so does heating with iodine; other attempts to reduce oleic acid to stearic acid have also been successful. For details of these and other new processes the reader is referred to the *Journal of Chemical Industry*, 1908, vol. 27, p. 489.

Recently it has been shown that when **Oleic Acid** is treated with nickel powder in the presence of hydrogen, it takes up hydrogen and gives an almost theoretical yield of hard stearic acid.

Moreover this latter action is of general importance. Not only does oleic acid, but also liquid *unsaturated fats* take up hydrogen under these conditions and become converted into hard substances. Thus the liquid glyceride, triolein, is converted into solid tristearin :—

$$C_3H_5(OOC.C_{17}H_{33})_3 + 3H_2 = C_3H_5(OOC\,C_{17}H_{35})_3.$$

Sabatier and Maihle (*Ann. Chim. Phys.*, 1909, [8], **16**, 73) showed that **oleic** and elaidic acids, when treated with hydrogen in the presence of *reduced* nickel at 280°-300° C., yielded stearic acid. The nickel, technically prepared by reducing nickel carbonate *in situ*, is thrown into the boiling fat and H gas is passed through.

Normann (English Patent, 1,515, 1903) caused the vapours of fatty acids, mixed with hydrogen, to pass over the catalytic metal distributed over a suitable support, such as pumice stone.

Recent work has been principally directed towards the preparation of the catalytic nickel in a suitable state, the best proportion of catalyst to use, the best temperature of hydrogenation, the proper refining of the fatty body, the application of continuous mechanical agitation, the purification of the hydrogen.

For details of these the reader must consult the patent literature above referred to. Published details are meagre. Crossley (*loc. cit.*) gives details for rape oil, whale oil, etc., which were published in the lawsuit of Joseph Crosfield & Sons, Ltd., *v.* Technico-Chemical Laboratories, Ltd.

The method was invented by Sabatier and Senderen. The reader will find a résumé of their researches in the *Annales de Chimie et de Physique*, 1905, [8], 4, 319; 1909, [8], 16, 70. See also *Sabatier, Ber.*, 1911, 44, 1984; Sabatier, "La Catalyse."

An excellent account is also given by Crossley, *The Pharmaceutical Journal and Pharmacist*, 1914, 92, pp. 604, 637, 676. See also *C. Ellis, J.S.C.I.*, 1912, 31, 1155; T. Shaw, *ibid.*, 1914, 33, 771.

The process has now become of great industrial importance, because so much of the natural supply of hard fats is now employed in the making of margarine and other food stuffs that the amount of such soaps available for soap-boiling has been seriously diminished.

One ton of oleic acid requires about 79,000 l. (2,800 cub. ft.) of hydrogen. One ton of triolein requires 75,900 l. (2,680 cub. ft.) of hydrogen.

The production of hydrogen for this purpose is described in Vol. II.

Water gas is liquefied and the hydrogen separated from the CO by fractional distillation. The gas used for hydrogenation consists of H = 95-97 per cent., CO = 2 per cent., rest = N. The pumping is done by a gas engine utilising the separated CO as fuel.

The hydrogen used must be free from H_2S, 0.1 per cent. being sufficient to destroy the catalytic activity of nickel.

In 1913 the Linde Co.'s plants for producing H for the hardening of fats (*Zeit. Angew. Chem.*, 1913, 26, III. 814; see also Vol. II., "Industrial Hydrogen"), yielded enough H to harden 100,000 tons of fat.

Whale Oil is the chief oil subjected to hydrogenation, the world's supply in 1912 amounting to 1,200,000 barrels (42,000 tons). (See *Offerdahl, Ber. deutsch. Pharm. Ges.*, 1913, 23, 558, who states that there is a factory in Norway capable of producing 4,500 tons of H by an electrolytic method, and of hardening 150 tons of whale oil per twenty-four hours.)

Hardened whale oil melts at 40°-50° C., is devoid of taste and smell, and so is a valuable fat.

Hydrogenated and hardened fats are at present used principally for **soap-making**. Although the soaps produced are hard and do not lather well, this difficulty could be got over by mixing the hardened fat with a suitable amount of another fat which would give the necessary qualities to the soap.

Hardened **Fish Oils** must have their iodine value reduced to under 50 if they are to yield a suitable washing soap, devoid of all smell of fish oil.

Hardened **cotton-seed oil** and hardened **whale oil** are stated to be used for edible purposes, and no doubt the use of hardened fats in this respect will greatly increase in the future.

However, an oil hardened by such a process, including Ni as a catalyst, usually contains 0.5-2 mgNi per kilo, and possibly deleterious effects might arise from the unlimited consumption of such oil. Normal and Hügel (*Halbmonatsschrift für Margarineindustrie*, 1913, VI., No. 17) showed that this quantity of Ni is often contained in food stuffs prepared in nickel vessels, which have had no injurious effects on persons who have consumed them.

X.—SOAP—MODERN MANUFACTURE AND ANALYSIS

By G. Martin, Ph.D., M.Sc.

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O. Kirchner.—"Die Kaustische und Kohlensaure Verseifung." Vienna-Leipzig, 1910.
Lewkowitsch, "Oils, Fats, and Waxes," and Wright and Mitchell, "Oils, Fats, and Waxes," give excellent summaries of soap-making.

Soaps are the metallic salts of fatty acids. The sodium and potassium salts of the fatty acids are soluble in water and constitute our ordinary "hard" and "soft" washing soaps respectively—although to-day certain sodium salts are manufactured which are quite soft, while certain potassium soaps possess a considerable degree of hardness, so that the old distinction between these classes of soap no longer holds accurately.

The soaps of other metals, *e.g.*, calcium, aluminium, magnesium, etc., are all insoluble in water, and so are quite useless for detergent purposes. Aluminium soaps (made by adding saponified linseed or cotton-seed oil to a solution of alum) are, however, used to impregnate waterproof material and to thicken oils; while lead and manganese soaps are used in varnish making (which see).

We may classify the processes employed in soap manufacture under three heads:—

1. *Soap-making processes where glycerol is set free and separated from the resulting soap.*
2. *Soap-making processes where glycerol is set free, but is not separated from the resulting soap.*
3. *Direct neutralisation of fatty acids with alkalis, no glycerol being produced.*

We will consider each in turn.

Soap-making Processes where Glycerol is set free and separated from the resulting Soap

When the natural oils or fats are boiled with caustic soda they are decomposed according to the equation:—

$$\underset{\text{Fat.}}{C_3H_5(O.CO.R)_3} + 3\underset{\substack{\text{Caustic}\\\text{soda.}}}{NaOH} = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + 3\underset{\text{Soap.}}{R.COONa}$$

The glycerol is recovered from the liquid which settles out below the soap.

This is the process employed on the largest scale at the present time. Measured

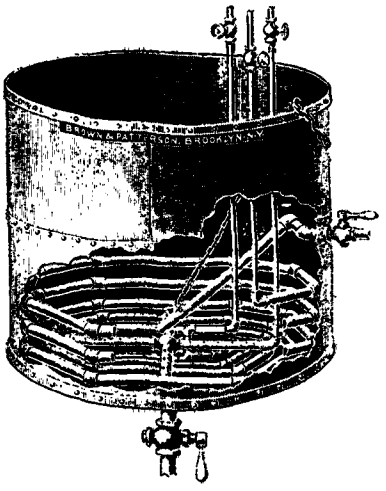

FIG. 30.—Soap Kettle, showing closed and open steam pipes, swivel-join outlet pi pe, and outlet valve. (Brown& Patterson, New York.)

amounts of oils and fats are run into a large cylindrical vessel, called a soap kettle, varying in diameter from 5-25 ft., and in depth from 8-30 ft., and fitted with an open steam coil for heating the contents, and a 3-in. outlet valve at the bottom for running off the lye. At the side is an outlet pipe of 3-4 in. diameter connected with a swing joint and a 3-in. cock, for transferring soap to the mixer or "Crutcher."

The proper amount of oil having been introduced, a dilute solution of caustic soda "lye" of 15° Be. is run in from the lye tank, steam is turned on, and the whole is vigorously boiled. As the caustic soda is taken up by the fat, more and more is added, care being taken, however, not to add it too quickly, for if present in excess it will retard the saponification. An excess of caustic soda, however, is required for the completion of the saponification.

The saponification takes place in three stages.

First an emulsion is formed, owing to the change :—

$$\begin{array}{l} CH_2.O(C_{18}H_{35}O) \\ | \\ CH.O.(C_{18}H_{35}O) \\ | \\ CH_2.O.(C_{18}H_{35}O) \\ \text{Tallow (tristearin).} \end{array} + 3NaOH = \begin{array}{l} CH_2.OH \\ | \\ CH.O(C_{18}H_{35}O) \\ | \\ CH_2.O.(C_{18}H_{35}O) \\ \text{Distearin.} \end{array} + C_{18}H_{35}OONa + 2NaOH$$

Soap.

Next a pasty mass is produced when the change has gone one stage further :—

$$\begin{array}{l} CH_2OH \\ | \\ CH.O.(C_{18}H_{35}O) \\ | \\ CH_2O.(C_{18}H_{35}O) \\ \text{Distearin.} \end{array} + 2NaOH = \begin{array}{l} CH_2OH \\ | \\ CH.OH \\ | \\ CH_2.O.(C_{18}H_{35}O) \\ \text{Monostearin.} \end{array} + C_{18}H_{35}.OONa + NaOH$$

Soap.

Finally a clear homogeneous mass appears in the kettle, which represents the complete saponification :—

$$\begin{array}{l} CH_2OH \\ | \\ CH.OH \\ | \\ CH_2.O(C_{18}H_{35}O) \\ \text{Tristearin.} \end{array} + NaOH = \begin{array}{l} CH_2OH \\ | \\ CH.OH \\ | \\ CH_2OH \\ \text{Glycerol.} \end{array} + C_{18}H_{35}.OONa$$

Soap.

In the clear mass there is present at this stage: soap, glycerol, some caustic soda in excess, some salt, sodium carbonate and sulphate (impurities in the caustic soda), and any unchanged animal tissue present in the fat. If saponification has been properly completed there should be no free or unsaponified fat.

Dry salt is now shovelled into the mass and scattered over the surface. Soap is but feebly soluble in a solution of brine, and so it separates out into a layer of soap above and glycerol water and excess lye below. The process is known as "graining" or "cutting" the soap.

A tallow or cotton-seed soap stock will be satisfactorily grained with 7-19 per cent. of salt in the stock lye. Cocoa-nut oil soap requires much more.

After each addition of salt the mass is well boiled up in the kettle, and the appearance of the soap noted. As water is withdrawn from the soap to dissolve the dry salt it loses its transparency and assumes a "grain-like" appearance. Finally

the neutral lye separates out below and the soap above. The addition of salt is now discontinued, and the contents of the kettle well boiled in order to intimately mix the lye.

Finally steam is turned off, and the lye allowed to settle out. The time required for this depends upon the size of the soap kettle. Sometimes two hours are sufficient, but usually the whole day is taken up in saponifying, and the lye allowed to separate overnight. The neutral lye is then run off at the bottom of the soap kettle, and is either pumped to the glycerol refinery, or stored until convenient for using. The curdy soap remaining in the kettle is again boiled up with water to form a homogeneous paste ("closed"), a strengthening charge of caustic soda is added, and the boiling continued, to ensure complete saponification, and at the same time to wash out impurity from the soap, for much colour is discharged into the alkaline lye. Finally, the lye is again separated by graining with salt as above described. This is known as the "pickle change."

Sometimes the soap is again treated in the same manner in order to remove impurities which spoil its colour—the impurities being discharged each time with the lye.

If the soap is to contain rosin, the "strengthening charge" of caustic soda is omitted and the rosin is added after withdrawing the second lot of lye. The rosin is added in fragments smaller than a man's hand, live steam being passed simultaneously through the grained soap. If added by hand, the addition of rosin continues over several hours, during which time only sufficient steam is needed to keep the soap hot and slowly melt the rosin. When all the rosin is added a considerable amount of lye at 20° Be. is run in and the mass vigorously boiled. Rapid combination ensues, and lye is added as required in order to prevent the soap from "closing" (*i.e.*, forming a homogeneous mass with the lye). Indeed, the soap must be kept "open" (*i.e.*, separated in a distinct layer from the lye) by the addition, if necessary, of more 20° Be. lye, and when no more of this is absorbed, with dry salt. With the soap "open" (separated from the lye) combination with alkali with rosin (an acid body) takes place rapidly, and an easy discharge of colouring matter into the waste lye beneath occurs. When the change is completed the highly coloured and impure lye (which contains practically no glycerol since this has been removed with the lye of the two previous operations) is run away down the sewer. Then sufficient water is added, with boiling, so as to just "close" the soap (*i.e.*, make it into a homogeneous paste with the lye), and then a strengthening charge of 20° Be. is added, with boiling, until the soap is again "opened" (*i.e.*, separated as a layer from the lye), the lye being added as fast as it is absorbed.

When the absorption ceases, the saponification is completed, and the whole is boiled. If the soap tends to "close," brine from 10° Be. to 20° Be. (according as the soap is thick or thin) is added. The lye separating should be alkaline ("strength lye"). After turning off steam the lye is allowed to settle out overnight, withdrawn, and (since it contains free caustic soda) used for treating another lot of stock, or added to the grained nigre or stock change of other boilings, where it assists in the saponification of fresh stock.

The soap must now be "fitted," *i.e.*, brought to the condition of finished soap. To do this, the strengthening lye is withdrawn, and the open soap is boiled up with water until the whole forms a homogeneous paste. Additions of water are now made very carefully, each addition of water being followed by a thorough boiling, and its effect noticed. The art of the soapmaker consists in so adjusting operations that the soap contains just the proper amount of water, and yet is still "open" enough to allow the intermingled aqueous solution and impurities (principally iron salts of fatty acids) to settle out.

Addition of water should cease when the soap boils up regularly with but little steam, and rolls over a stiff surface, breaking into saucer-like depressions which retain their firmness and transparency from the centre to the circumference of the kettle. Much experience is required to produce the proper degree of hydration.

Soft-bodied stock (grease, cotton-seed oil, heavily rosined tallow) and firm stock (tallow and cocoa-nut oil) for unfilled soaps such as Castile, floating soap, and milled soap base, require but little water, whereas soap intended to be filled with soda-ash solution, or tallow soap slightly rosined, require much water.

If the soap is to be quite neutral, a little cocoa-nut oil may be added towards the close and well boiled through. This effectively neutralises the free alkali, and greatly improves the finished soap. Sometimes "oleic acid" (red oil) or melted stearic acid is added for the same purpose.

When brought to the proper degree of hydration, the mass is allowed to settle for some days, when there is found at the bottom of the pan a very small amount

of alkaline solution, above which rests a layer of dark soap called "nigre," and above this rests the bulk of the finished soap ("neat soap"), covered on the top by a thin layer of solidified soap in a spongy condition, owing to air bubbles

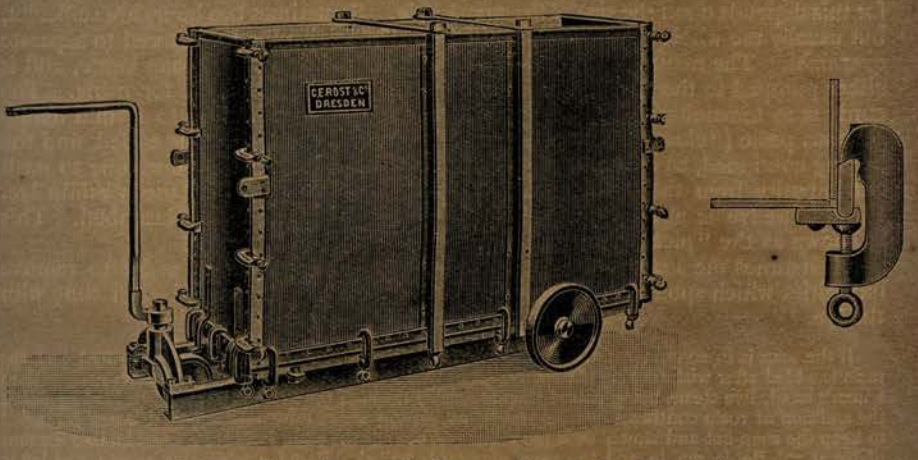

FIG. 31.—Soap Frame, with Clamp. (Rost & Co., Dresden.)

which have risen from below during the settling process. The "nigre" owes its dark colour to metallic soaps—usually iron ones—and contains caustic soda and excess of salt. Its volume varies between 25-35 per cent. of the mass. The

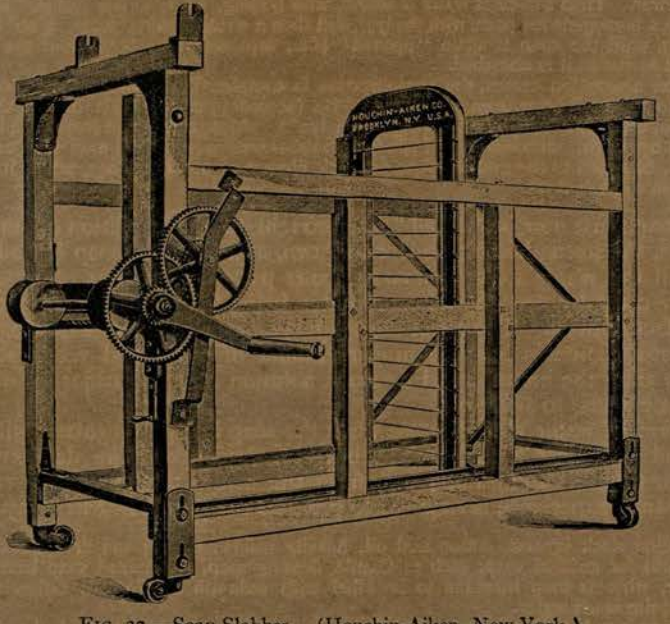

FIG. 32.—Soap Slabber. (Houchin-Aiken, New York.)

"neat" soap above the nigre should be practically neutral. The line of demarcation between the good soap and nigre is sharply defined.

If the soap is to be used pure, the "neat" soap is run directly whilst warm into

soap frames. These are iron plate boxes on a wooden base mounted on wheels, with detachable sides, and capable of holding from 12-15 cwt. of soap.

In some cases frames are made as high as 72 in.; the reasons for this are obvious. There are tops and bottoms in every case, and whether the frame is 30 in. or 72 in. high, the tops and bottoms are exactly the same thickness, and consequently much more remelting has to be done for the amount of soap turned out from a low frame than from a high one.

On cooling, the soap in the frame hardens and solidifies; the iron sides are then detached and the solid block of soap cut first into slabs either by a workman drawing a pianoforte wire through the block at intervals, or, more rapidly, by means of a machine called a "slabber."

When slabs of uniform thickness are required, a slabber such as that illustrated is usually used. But where slabs of various thicknesses are required, either a simple pianoforte wire, or still better, a hand machine, is used for cutting one slab at a time.

The slabs of soap are then cut into bars by placing in another machine in which a number of parallel wires attached to a movable frame are forced simultaneously through the slabbed soap, thus cutting it into pieces usually weighing 3 lbs.

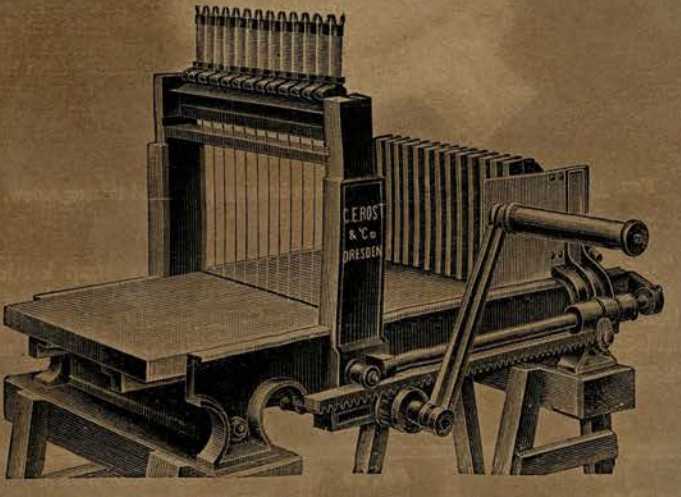

FIG. 32a.—Bar-Cutting Machine. (Rost & Co., Dresden.)

Sometimes the bars of soap thus produced are stamped into cakes in special presses. This is always done with toilet soaps (which see). Fig. 35, p. 111, shows a typical hand press.

If, however, the soap is intended to be "*filled*," *i.e.*, mixed with excess of sodium carbonate solution or with sodium silicate—substances much used in producing the cheaper sorts of soap, and having themselves considerable detergent qualities—or if perfumes and colouring matters are to be mixed with the soap, then the soap is first run into a mixing machine (called a "crutcher") and is there incorporated with the necessary materials by means of mechanical stirrers or screws (Fig. 33). After "crutching" for a sufficient time (sometimes with artificial heating in a steam jacket with which most crutchers are provided), the soap is finally run out into frames placed below the crutcher, and then the framed soap is cooled into blocks, slabbed, and the slabs cut into smaller pieces in cutting machines as previously described.

Since these frames, when filled with soap, often weigh considerably over half a ton, the floor of the factory should be of iron plate $\frac{3}{16}$ to $\frac{1}{4}$ in. thick, in order to avoid splintering the woodwork, and to facilitate the running of the heavy frames from one part of the works to another. Concrete floors are not advisable as they soon break up. Fig. 34 shows a conventional view of a soap factory.

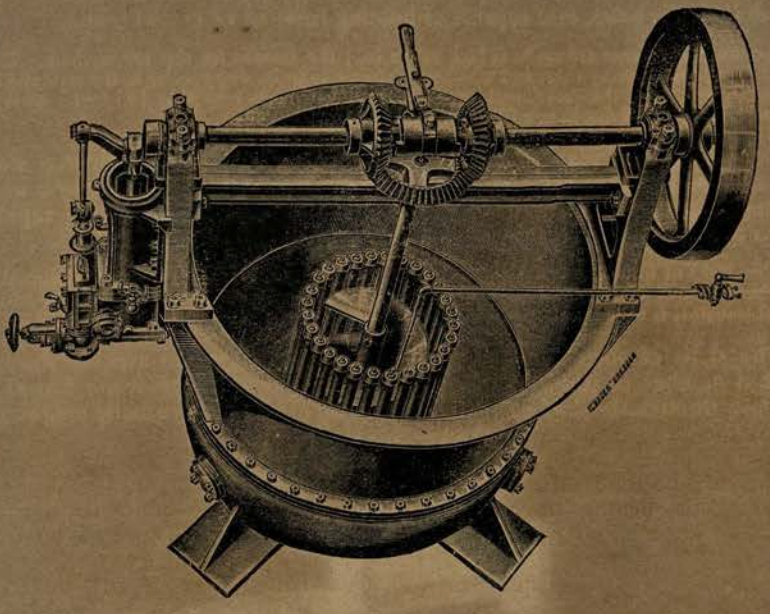

FIG. 33.—Soap Crutcher, showing steam-heating pipes and mixing screw.

The "nigre" or impure soap remaining behind in the soap kettle after the "neat" soap is run off is boiled up with steam and grained by throwing in dry salt and boiling. On settling, the lye underneath is run into the sewer while the nigre is utilised for adding to other soap stock, or used as a base for milled soap or floating soap.

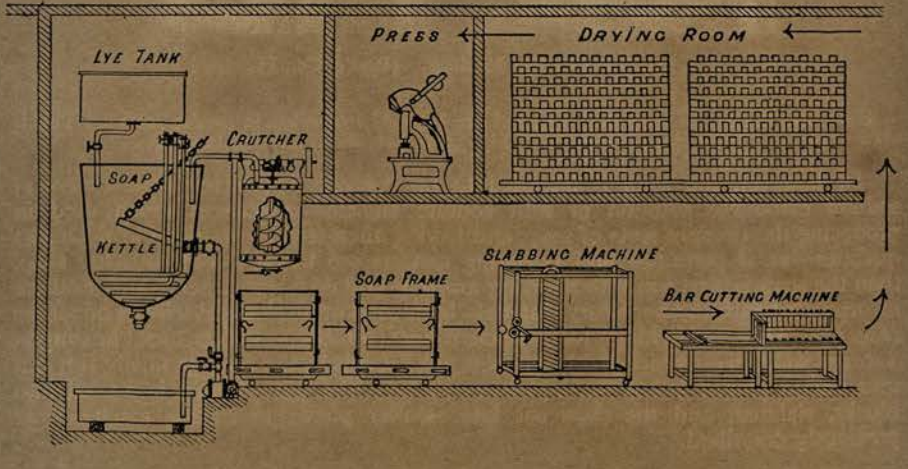

FIG. 34.—Conventional View of a Soap Factory, showing the course of manufacture from the Soap Kettle to the Pressed Tablet.

Soap-making Processes where the Glycerol is set free but not separated from the Soap

These processes suffer from the economic disadvantage that the glycerol—a valuable product—is retained by the soap, and so is lost. They may be divided into three classes: (*a*) **Cold Process Soaps**; (*b*) **Hydrated Soaps** (which include "marine") and "**Soft**" **Soaps**; (*c*) **High Pressure Soaps**.

(*a*) **Cold Process Soaps.**—Certain fats, principally those of the cocoa-nut oil and castor oil group, have the valuable property of being directly converted into soap at ordinary temperatures when mixed with concentrated caustic soda (sp. gr. 1.33, or 66° Twaddel, containing 24 per cent. NaOH), thus forming "Cold Process" soap.

The fat is weighed into an iron vessel provided with stirring apparatus, and is brought to the proper temperature (65° C. in cold weather, 50° C. in hot), and then the calculated amount of concentrated caustic soda or potash (or a mixture of both) is rapidly run into the vessel, and the whole thoroughly stirred until the soap begins to thicken.

If fillers are to be used, the intended amount of scent, sodium silicate, and sodium or potassium carbonate solution ("soda-ash lye" or "pearl ash") is now stirred in; the mixture becomes thinner, and after a few minutes becomes thick. The paste is then run out into a wooden frame, and well covered up to keep in the heat. Combination proceeds in the frame, considerable warmth is evolved, and the mixture swells up, soap being gradually produced according to the equation:—

$$\underset{\text{Fatty oil.}}{C_3H_5(O.CO.R)_3} + \underset{\substack{\text{Caustic}\\\text{soda.}}}{3NaOH} = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Soap.}}{3R.COONa}$$

R represents the radicle of the fatty acid.

With small batches the process may be complete in two days. Usually, however, a week or more is allowed to elapse.

The great disadvantages of the "Cold Process" method are:—

1. Complete combination of fat and alkali are seldom secured; such soaps usually contain free alkali and unchanged fat.

2. The glycerol—a valuable commercial product—is retained in the soap and so is lost.

The advantages are: great simplicity in plant and operation; great rapidity of production.

The amount of soap—principally cheap scented toilet soap—made by this process is small. Some transparent soaps are also made this way.

(*b*) **Hydrated Soaps, Soft Soaps.**—**Soft Soaps** (see p. 117) are prepared by boiling together caustic **potash** and suitable oils at ordinary pressures until a sample when cold sets to a clear translucent mass. The mass is then boiled down until sufficiently concentrated and is put up in barrels, canisters, or drums for sale. They form soft, jelly-like masses. **Hydrated** soaps are manufactured in the same way as soft soap, but **caustic soda** is used instead of potash, and the fatty materials so chosen as to yield **hard opaque products**. **Marine soaps** (which see) are made this way from cocoa-nut oils (p. 116).

In order to produce a practically neutral soap, the quantity of caustic soda required for saponification must be carefully calculated from the saponification value of the fatty material employed. If proper quantities are taken it is quite possible to produce a practically neutral soap by careful working.

It is remarkable that other oils and fats, *e.g.*, tallow, which alone cannot be saponified in the cold by concentrated caustic soda solution, are readily saponified when incorporated with oils of the cocoa-nut oil group, the heat which is evolved on the saponification of these latter oils apparently aiding the conversion of the former into soap. The process is essentially a rapid one. Lamborn states that for a 1,000-lb. frame the caustic soda must be run into the fat in one and a half to two minutes, the silicate in the same time, and the stirring ("crutching") must be rapid and thorough for twelve to sixteen minutes. It is sometimes done by hand.

Every manufacturer employs his own formula. Two typical ones for hard crutched cold process soap are :—

No. 1.	No. 2.
75 lbs. tallow.	75 lbs. tallow.
25 lbs. cocoa-nut oil (Ceylon).	25 lbs. cocoa-nut oil.
75 lbs. caustic soda lye, 35·5° Be., made from 74 per cent. caustic soda.	70 lbs. caustic soda lye, 35·5° Be., made from 74 per cent. caustic soda.
125 lbs. "N" silicate of soda.	100 lbs. "N" sodium silicate.
20 lbs. potassium carbonate solution, 36° Be.	17 lbs. potassium carbonate lye, 36° Be.
Yield—320 lbs. soap.	Yield—288 lbs. soap.

When cold and hard the soap is taken out of the frame and cut into bars and pressed into tablets in the usual way (see pp. 104, 105).

(*c*) **Hydrated Soaps prepared under Pressure.**—Here the fatty matters and caustic soda are simply heated together under high-pressure steam in autoclaves, the object being to cause the reaction to occur at a more elevated temperature and pressure in order to shorten the time of reaction and to simplify the procedure. In some processes the caustic soda and fat are pumped continuously into the boiler, and the finished soap pumped out simultaneously through a weighted exit valve, the process being a continuous one. **Bennet & Gibbs** use **sodium carbonate** solution, which, at a steam pressure of 15-20 atmospheres, corresponding to 190°-215° C. in the autoclave, readily saponifies the fat.

Soap Making by Direct Neutralisation of Fatty Acids with Alkalis

These processes are growing in importance.

Since soaps are simply salts of fatty acids, obviously the most direct and simplest way to produce them is to directly neutralise the free fatty acids with caustic alkali or alkaline carbonates.

If **caustic soda** is used the process is very simple. The caustic soda is placed in a mixing machine ("crutcher"), the stirring apparatus set into rapid motion, and the fatty acids added in a rapid stream so that the entire charge is added in two to three minutes. Combination takes place thus :—

$$\underset{\text{Fatty acid.}}{R.COOH} + \underset{\text{Caustic soda.}}{NaOH} = \underset{\text{Soap.}}{R.COONa} + \underset{\text{Water.}}{H_2O}$$

R represents the radicle of the fatty acid.

After five to ten minutes the mixture thickens, and "filling" (such as sodium silicate or sodium carbonate) is added. The temperature must not exceed 60° C. The mixing ("crutching") should proceed rapidly for fifteen to thirty minutes, the temperature being maintained between 60° C. and 70° C. by means of steam in the jacket with which the mixing machine is provided. The soap is then run into frames and allowed to cool.

A slight excess of alkali is necessary for complete combination. For certain textile soaps this does not matter. If a grained neutral soap is required the soap may be salted out with brine, and "fitted" as described on p. 103. In practice the fatty acid is always run into the alkali, and not *vice versâ*, otherwise lumps are formed and the reaction does not proceed so smoothly.

If **sodium carbonate** is used instead of caustic the process becomes more troublesome; CO_2 is evolved thus :—

$$\underset{\text{Fatty acid.}}{2R.COOH} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Soap.}}{2R.COONa} + \underset{\text{Carbon dioxide.}}{CO_2}$$

The CO_2 liberated is a source of trouble, since it causes the liquid to froth up, and consequently the mixing pan must be fitted with a large movable "curb"—a barrel or funnel-shaped top—in order to retain the froth, and the heating must be carried out slowly to prevent frothing over. The solution must be boiled until all the

sodium carbonate has been neutralised and the CO_2 gas expelled. Then caustic soda is added and the soap boiled until it no longer absorbs more. Finally the soap is grained out with salt in the ordinary way.

Sodium carbonate is cheaper than caustic soda, nevertheless most manufacturers prefer caustic soda—especially as it is now manufactured so cheaply by electrolytic and other processes—since they consider that the slight saving in cost by using sodium carbonate is more than outweighed by the increased trouble and expense of working.

The fatty acids employed until recently were almost entirely confined to the "red oils" of the candle-maker (*i.e.*, oleic acid), and the resulting soaps were used for textile purposes and as the basis of certain soap powders. Within recent years, however, fatty acids have been obtained by first decomposing the fats and oils constituting ordinary soap stock by "*Twitchell's*" or some similar process (see p. 92), and the glycerol recovered; then the fatty acids so obtained are converted into soap by direct neutralisation as above described.

The great advantages of this latter method (which will in the near future probably entirely displace the older processes of soap-making) are (1) the glycerol is recovered from the fats *before making them into soap*, being immediately obtained in a concentrated and fairly pure form, which permits of its being worked up into the pure product far more easily and economically than when obtained from the impure soap lye of the ordinary method of making soap by boiling fats with alkalies. (2) The resulting operations of combining the fatty acids with caustic soda are rapidly and easily performed.

Fatty Acids are especially well adapted for making soft soaps with potash, for the glycerol in the original fat is recovered before treating the fatty acid with potash (see Twitchell's Process). In the ordinary way of making soft potash soaps by treating a neutral fat with potash and boiling down, all the glycerol is retained in the soap and so is completely lost.

Other Methods of Soap-Making.—Many attempts have been made to saponify fats or oils with lime, thereby producing an insoluble Ca soap + glycerol water, filtering off the glycerol water and working it up for pure glycerol; then converting the insoluble Ca soap remaining into ordinary soap by treating with Na_2CO_3:—Ca soap + Na_2CO_3 = soda soap + $CaCO_3$, and filtering off the precipitated $CaCO_3$. This is *Krebitz's Process*. See Krebitz, English Patents, 4,092, 1905; 4,092A, 1905. **Barbé** and **Garelli** (English Patent, 12,210, 1907) heat fats with ammonia under pressure, thereby producing ammonium soaps and glycerol. The ammonia soaps are now decomposed by steam, the ammonia being boiled off, condensed, and used again. The free fatty acids float on the surface of the glycerol water and are separated by decantation and converted into soap by direct treatment with NaOH; or the ammonia soaps are directly decomposed by a sodium salt:—$2NH_4$ soap + Na_2SO_4 = sodium soap + $(NH_4)_2SO_4$ (see pp. 93, 99).

Characteristics of Soap made from Different Classes of Soap Stock

Soap stock may be divided into the following classes, all of which exhibit well-defined chemical and physical differences:—

CLASSIFICATION OF SOAP STOCK

1	2	3	4	5
Cocoa-nut oil.	Olive oil.	Tallow.	Castor oil.	Red oil.
Palm-kernel oil.	Olive oil foots.	Greases.	Linseed oil.	Rosin.
...	Cotton-seed oil.	Palm oil.	...	...
...	Pea-nut oil.	...	...	...
...	Sun-flower oil.	...	...	...
...	Corn oil.	...	...	...

Class 1. Cocoa-nut and Palm-kernel Oils.—These oils saponify with great rapidity at ordinary temperatures with cold concentrated caustic soda or potash, with the evolution of much heat. This property peculiarly adapts them for soap manufacture by the cold process. Weak caustic soda solution, 12° Be.,

such as is used in the saponification of tallow, scarcely affects these oils in the cold, while lye of 20° Be. at least is required for making them into soap by the boiling process. These oils are characterised by the large amounts of glycerides of low molecular weight they contain; consequently they absorb more alkali and liberate more glycerol (12 per cent.) and give a firmer and higher yield of soap than any other oils used in soap-making. The addition of cocoa-nut oil to tallow and cotton-seed oil in manufacturing settled ("grained") soap, yields a soap much superior to that produced from either stock alone.

Cocoa-nut oil soap is white, hard, and brittle, and gives a quick, profuse, but thin lather with both salt and fresh water. The soap is capable of absorbing enormous amounts of water and mineral matter ("filling," such as sodium carbonate and sodium silicate), yielding a firm soap. It requires a very large amount of salt to throw it out of solution, being very soluble both in fresh and salt water, and thus is a "marine" soap. A 50 per cent. cocoa-nut oil soap requires 15-20 per cent. of salt in the stock lye to throw it out of solution, against 7-10 per cent. required for ordinary tallow stock. The graining of pure cocoa-nut oil soap with salt is very unsatisfactory. Such soaps, unless very carefully saponified, become rancid with age.

Class 2. Olive, Cotton-seed, and Corn Oils.—All these oils consist principally of olein—the glyceride of oleic acid.

Olive oil saponifies readily with lyes of very different densities, yielding a greenish-coloured soap, called "Castile," which gives a thin, slimy but abundant lather peculiar to all soaps containing much oleate. The soap is an ideal one for toilet or textile purposes, but is very expensive. **Refined cotton-seed oil** saponifies with difficulty, yielding a soap which, unless very carefully saponified, suffers a very rapid deterioration, becoming discoloured and rancid on keeping. Containing much olein, the oil yields a thin soap lacking the body of tallow soap; by mixing with large proportions of soda-ash and sodium silicate, a firm soap is produced, which is much used in the United States as a laundry soap.

All soaps consisting principally of sodium oleate (for example, olive-oil and cotton-oil soaps) are much more soluble in water than soaps made from tallow, and therefore containing much sodium stearate. Moreover, such oleate soaps readily absorb moisture from the air, and thus give rise to "sweating." The yield of glycerol is about 10 per cent.

Class 3. Tallow, Palm Oil, Greases.—The principal glycerides present are stearin and palmitin. Tallow is readily saponified with weak lye, between 10°-15° Be., and yields a firm soap of good body, and easily grained by 7-10 per cent. of salt in the lye. The soap is one of the least soluble, and it yields an inferior but persistent lather, excellent for shaving purposes, but overlooked by the public, who demand a freely lathering soap. On ageing, tallow soap becomes so hard that it may injure fabrics. It is best mixed with other stock, imparting body and firmness to the resulting soaps. **Palm oil** contains much palmitin, and in general properties produces a soap much like tallow soap. It yields a slow but thick and lasting lather. Is a good textile soap. These oils yield about 9 per cent. of glycerol.

Class 4. Linseed and Castor Oils are very readily saponified, yielding a quick-lathering, very soluble soap, of pale brown colour and characteristic odour. The oils are used for making transparent soaps and for the green *Sapo verdigris* of pharmacy.

Class 5. Red Oil and Rosin.—Red oil is commercial oleic acid, and consequently directly combines with caustic soda or sodium carbonate to produce the soap sodium oleate. Red oil, or olein soap, is much used in the textile industry, being similar to the soaps discussed under Class 2 (which see). **Rosin** is also an acid body, and consequently directly combines either with caustic soda or sodium carbonate to produce a soap which, although possessing valuable detergent properties, is very hygroscopic, very soluble in water, and soft. The presence of rosin in other soaps is betrayed by a stickiness and a readiness to "sweat." Rosin soaps added to tallow soaps modify their hardness and improve their properties for many purposes. Rosin must not be used as a constituent of textile soaps (which see, p. 114).

Various Kinds of Soaps

Milled Soap, Toilet Soap.—The best toilet soaps are manufactured by the process of milling, whereby they acquire a finish and quality otherwise unattainable. Soaps thus manufactured are certainly the most economical, since they contain no moisture and consequently do not shrink or lose weight (as do all toilet soaps not milled). Moreover, they improve on keeping — other soaps usually deteriorating. The soap must be a grained, settled soap, of good quality, and perfectly neutral (0.3 per cent. Na_2CO_3 and 0.5 per cent. NaOH are the utmost limits allowable). The racked and fairly dry bars of soap are cut into shavings by a rotatory cutting machine ("soap-chipper") and these are dried by steam in a drying-room until the water is reduced from 30 per cent. (the usual amount in freshly made soap) to anything between 14 per cent. and 3 per cent.

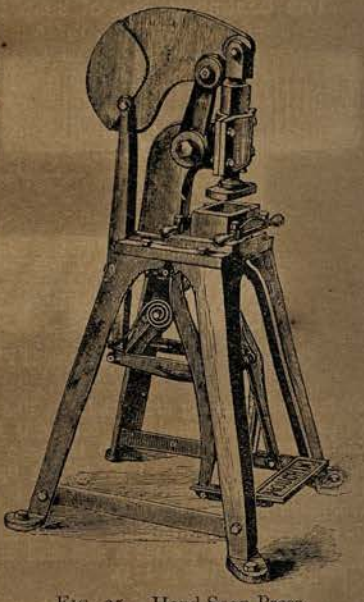

FIG. 35.—Hand Soap Press. (Houchin, New York.)

The dried shavings are then mixed with the necessary colouring matters and perfumes in a zinc-lined box, and then are ground in a **Toilet Soap Mill,** which consists of polished stone rollers of the best Quincey granite, arranged horizontally or with a pitch as shown.

The soap as it comes from the last roll is detached by a knife, and comes out as translucent homogeneous ribbons of the thickness of paper. Three or four millings are enough for a cheap soap, and seven or eight for better quality soaps. From the mill the mass of soap ribbons is fed into the "plodder," where, by means of a spiral screw, the mass is forced under great pressure through a number of holes in a plate, so that the soap passes this part of the machine in the form of a number of thick threads, which are again squeezed

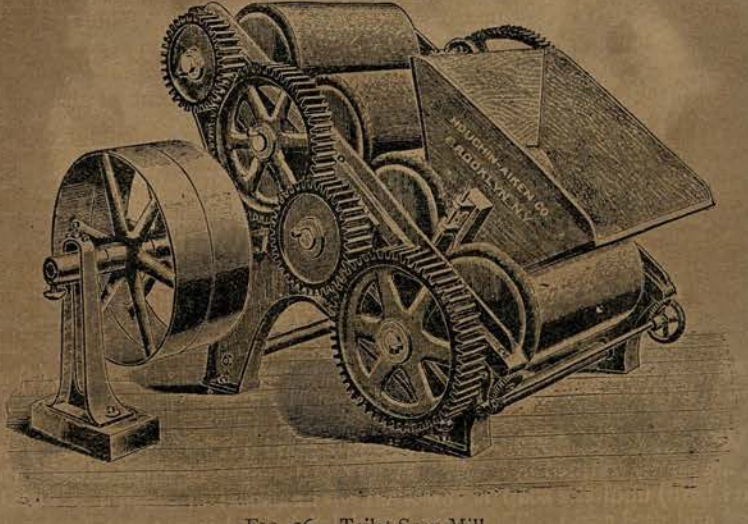

FIG. 36.—Toilet Soap Mill.

together and coalesce to come out of the plodder mouth in the form of a continuous bar. Sometimes it is necessary to warm the mouthpiece of the plodder (which is provided with a water jacket and a small Bunsen burner) in order that the soap may be somewhat softened and thus pass through the perforations of the disc without being broken by successive revolutions of the screw.

The best plodders are porcelain lined.

The continuous bar of soap is cut automatically as it comes forth from the plodder into pieces, each weighing about 4 oz., which are then rapidly stamped in presses into the oval tablets in which toilet soap is sold.

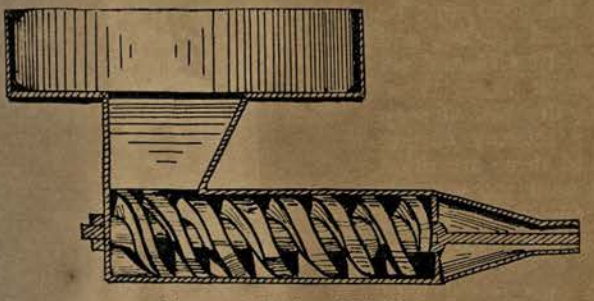

FIG. 37.—Section of Plodder.

Continuous Soap-Drying Apparatus. — The process of toilet soap-making, as described above, requires at least seven days. The period may be reduced to only ten to fifteen minutes by employing the special machine illustrated in Fig. 39, whereby the lengthy processes of framing, slabbing, cutting, drying and chipping are avoided. The fluid soap, just as it comes from the kettle or crutcher (where it is perfumed and coloured) is poured down a hopper surrounding a series of water-cooled cylinders, from which the soap as it cools and solidifies is detached by knives in the form of thin shavings; then, falling upon a series of endless belts of wire cloth enclosed in a chamber through which dry hot air is continually driven, is rapidly dried, and dropping upon successive layers of underlying and moving belts, is finally discharged with its water reduced to 12 per cent. in a few minutes. The dried chips are then passed on to the mill and plodder in the usual way. This machine is also used on the large scale for the manufacture of "soap chips" and "soap powder" (see p. 115).

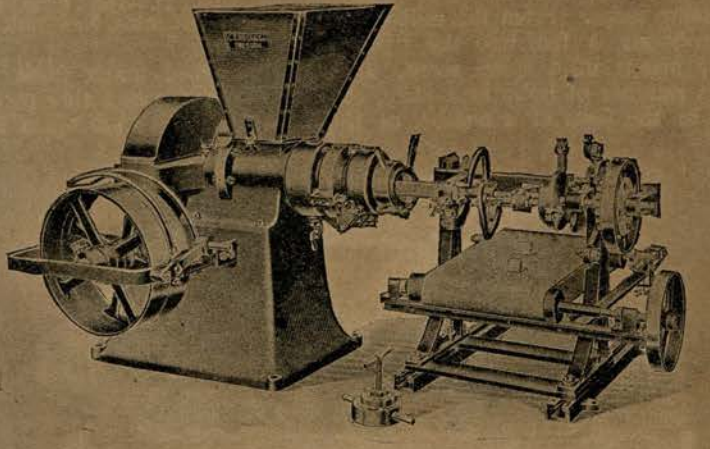

FIG. 38.—Plodder, showing automatic arrangement for cutting the bar of soap into small pieces for stamping. (Rost & Co., Dresden.)

Transparent Soaps may be made by mixing soap with (1) alcohol, (2) alcohol and glycerol, (3) alcohol and sugar, or (4) sugar alone.

1. With Alcohol Alone.—Shavings of a good quality soap, carefully dried in hot air, are gently warmed in a still with an equal weight of rectified spirit (heating on water bath) until the soap is dissolved. The excess of alcohol is distilled off, collected and used again. The clear liquid left behind is run into frames, cooled,

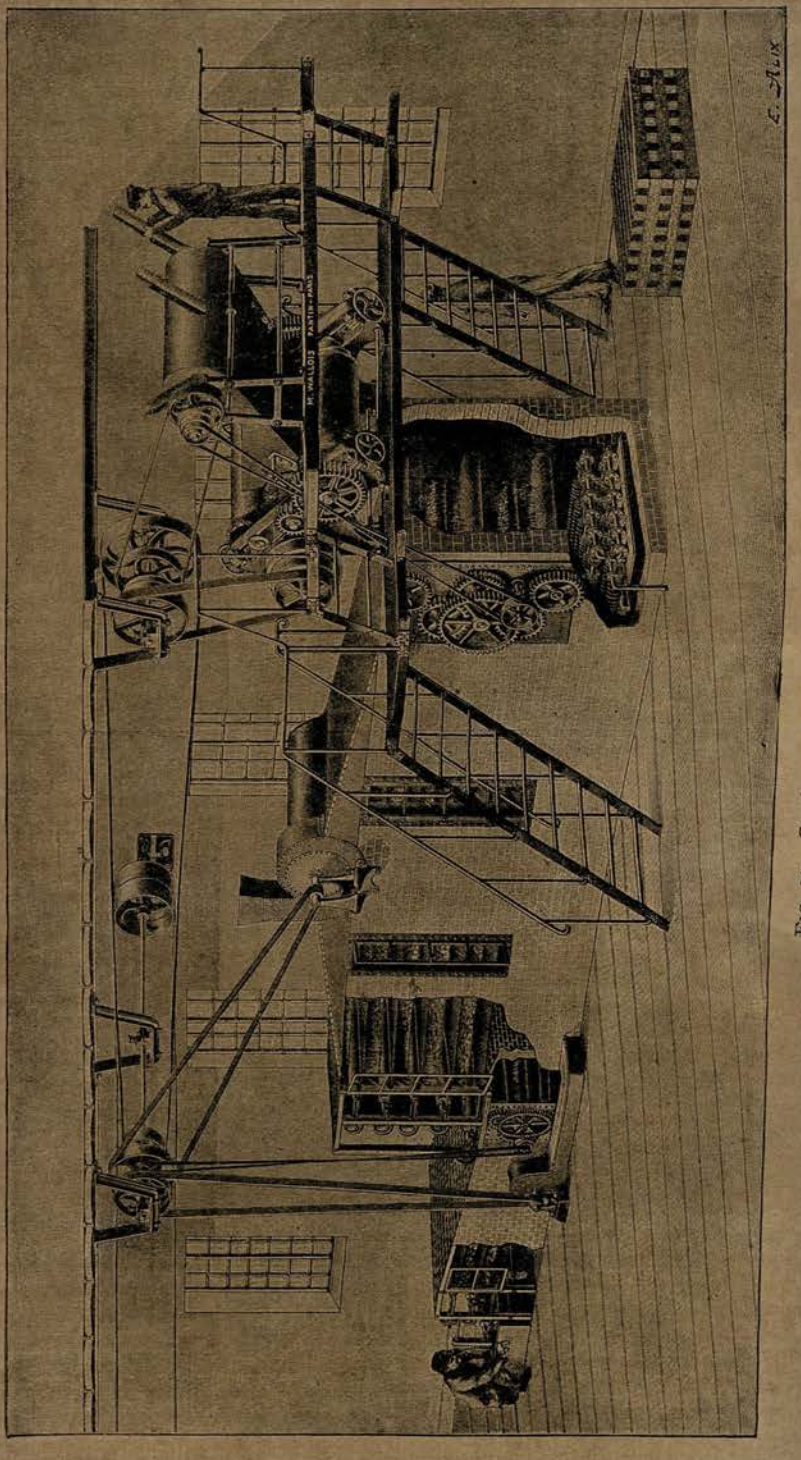

FIG. 39.—Continuous Soap-Drying Apparatus

cut into pieces, pressed, and allowed to season in dry air. The best, but most expensive, soap is thus produced.

2. With Alcohol and Glycerol, or Sugar.—These and the succeeding classes of soaps are best made by the "cold process," from about equal parts of cocoa-nut oil and tallow, together with a quantity of castor oil; the latter oil greatly conduces to the transparency and at the same time diminishes the quantity of alcohol, glycerol, or sugar needed for transparency.

The melted ats are placed in a steam-jacketed crutcher, heated to 50° C., and the proper amount of lye at 38° Be. mixed in. On standing for over three hours the temperature rises spontaneously to over 80° C. Any glycerol is mixed in before adding the lye. Alcohol should be mixed in after the addition of lye and before allowing the mixture to stand. After the period of standing is over, sugar and soda-ash solutions at 80° C. are run in and vigorously mixed. After this, the mass is allowed to stand while samples are taken. Finally the soap is run out into frames, being strained as it does so. When cold and solid it is cut and pressed.

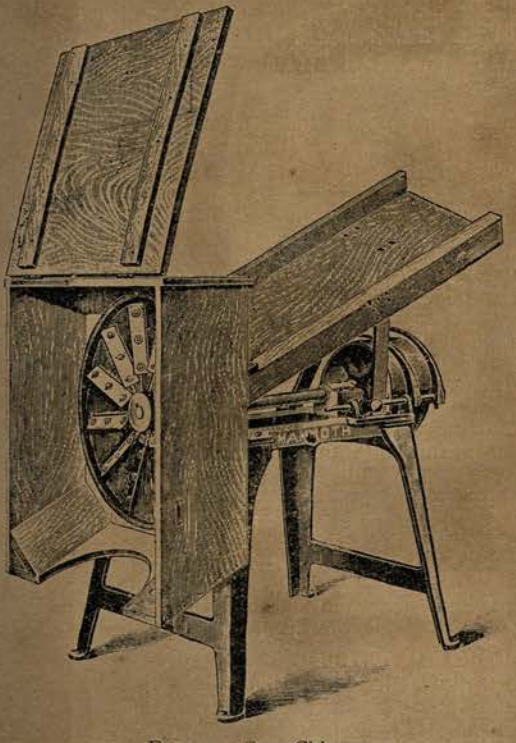

FIG. 40.—Soap Chipper.

The following is a typical formula for an alcohol-glycerol transparent soap: Cocoa-nut oil, 100-120 lbs.; edible tallow, 100-60 lbs.; caustic soda lye of 38° Be., 100-90 lbs.; alcohol (95 per cent.), 80-60 lbs.; glycerol, 40-60 lbs. This also is an expensive soap, but a cheaper transparent soap containing **alcohol and sugar** may be made from the following ingredients: Edible tallow, 100 lbs.; cocoa-nut oil, 100 lbs.; castor oil, 30 lbs.; alcohol (95 per cent.), 100 lbs.; sugar, 25-60 lbs.; water, 40-65 lbs. In cheaper soaps a quantity of soda-ash solution is added.

A still cheaper transparent soap, **without alcohol**, but containing **sugar** and castor oil, is as follows: Cocoa-nut oil, 100 lbs.; edible tallow, 80 lbs.; castor oil, 103 lbs.; sugar, 80 lbs.; caustic soda lye of 38° Be., 146 lbs.; soda-ash solution of 36° Be., 40 lbs.; water, 85 lbs. In the absence of alcohol and glycerol, the proportions of sugar and castor oil are increased in order to attain transparency.

Textile Soaps

A Soap for Scouring Raw Wool must dissolve freely at 50°-55° C., be quite neutral (free alkali deteriorates wool), free from uncombined fat, without rosin, sodium silicate, mineral oil, or other filling material. It should not contain more than 30 per cent. water, must be free from nitrobenzene or other perfuming stuff; it must not have an unpleasant smell when rubbed in the palm of the hand. A neutral soda soap, made from red oil (oleic acid) and sodium carbonate, is much used. A neutral olive-oil potash soap is best, but too expensive except for the very best quality goods. Cocoa-nut and cotton-seed soaps are useless unless they are quite free from odour, which otherwise persists in the finished goods. Cotton-seed and corn-oil soaps (made from semi-drying stock) are difficult to remove,

impart cloudiness to the milled wool, as well as causing odour and stickiness. Palm-oil soap is superior to pure tallow soap, the latter being somewhat insoluble.

A Silk Textile Soap must contain no free caustic soda or potash, but may possess a very slight degree of alkalinity due to a trace of sodium or potassium carbonate. A neutral potash soap from olive or lard oil is often used, as well as the cheaper soda olive-oil soap, and hard or soft palm-oil soap. Tallow soaps are unsuitable, as also are cotton-seed oil soaps. Soaps made from red oil (oleic acid) are suitable.

A Cotton Textile Soap, for which there is little demand, may contain dilute alkalis, since cotton is not injured by dilute caustic soda.

A Soap for Printers' Use must be fairly soluble in water, and so palm, olive, and cocoa-nut oil soaps are used instead of tallow soap. Such soap must be quite neutral, since free alkali may alter the colours or cause them to "bleed." Rosin, cotton-seed oil, and linseed-oil soaps cause colours to bleed, and so are unsuitable. Also the soaps must not impart any odour to the cloth.

A Soap for the Woollen Dyer may be made from tallow, palm, or olive oil, and be of a very slight degree of alkalinity. Before woollen cloths or yarns are dyed any oil they contain must be removed by soaking them in a very common soap, usually made from bone fat and cotton-seed oil, and slightly alkaline in reaction.

Soap Powders, Dry Soaps, Washing Powders.—Soap powder supplies the demand for a cheap quick detergent for cleansing coarse articles. It is a mixture of soap (usually made from low-grade grease) and soda-ash. The soda-ash takes up water of crystallisation, and this dries the soap. Without the addition of the soda-ash it is difficult to produce a true soap powder from pure soap. Rosin cannot be used, because, owing to the deliquescence of rosin soap, the soap powder becomes lumpy. The soap, grained, separated from the waste lye, closed, and finished very thin, is run directly from the kettle into the mixing machine (crutcher), and then the sodium carbonate (soda-ash) added in successive amounts until the proper quantity is present, and finally the sodium silicate is usually added. The usual proportions are: 600 lbs. soap, 600 lbs. soda-ash, 100 lbs. sodium silicate. After mixing thoroughly, the mass is run into frames in the usual way; in some establishments it is poured in a layer over the floor, and the mass, when cold and firm, is broken into lumps, which are then smashed into small pieces in a disintegrator, and finally the fragments are ground to a fine powder in a special mill, and the powder stored either in casks or in cardboard cartoons. Sometimes sand, sodium sulphate, fullers' earth, talc, etc., are added to soaps of this nature.

A rapid method of manufacture, now adopted in most large establishments, is to pour the fluid soap direct from the crutcher into the hopper of the continuous soap-drying machine described on p. 112, whereby the soap is discharged, dried and disintegrated, ready for grinding, in ten to fifteen minutes from the time of entering the machine. Thus the tedious processes of framing, cooling, slabbing, etc., which occupy several days, are entirely avoided.

Peroxide Soaps.—Many efforts have been made to manufacture soaps containing active oxygen, as such soaps have valuable disinfecting and bleaching properties. Thus Henderson (English Patent, 14,784, 1906) treats cocoa-nut oil, prior to the manufacture of soap, with ozonised air, and the soap made with the product has an oxidising and antiseptic action, and is free from a cocoa-nut smell.

Wolffenstein (English Patent, 16,823, 1908) produces **non-alkaline** soap preparations containing oxygen as peroxide by causing free fatty acids to act at 100° C. upon alkali salts of peracids, such as sodium percarbonate, perborate, persulphate, etc. It is very remarkable that the salts of the peracids are stable enough to be used thus. The soaps have bleaching and disinfecting properties.

Byx (English Patent, 7495, 1909) dehydrates sodium perborate, and mixes it with fatty acids. The product is said to be stable. See also English Patents, 15,900, 1907; 7,619, 1909.

These methods promise to become industrially important.

Scouring Soap Base is best made from cocoa-nut oil. The glycerol, amounting to over 12 per cent., should be separated. Cocoa-nut oil requires for saponification by the boiled process caustic lye of at least 20° Be. The oil is first added to the kettle, then much lye at 20° Be. is run in. Saponification rapidly ensues. If too little lye is present the mass tends to thicken in the kettle; in this case more steam is admitted and lye rapidly added. Towards the end of the operation lye at 25° Be. is added Cocoa-nut oil soap requires more salt to grain than ordinary soap, and may on the first boiling be grained with strong lye up to 35° Be., and the lye (strongly alkaline) separated may be used for saponifying a fresh quantity of oil. The second graining is with salt. Then the soap is closed with water, grained with 20° Be. lye, boiled as on the strengthening charge, the lye withdrawn, and the soap finished by adding water, when it is ready to be used for mixing.

Castile Soap is made by settling a pure olive-oil soda soap. Owing to the high price of olive oil it is usually, in part, replaced by pea-nut, cotton-seed, or light-coloured red oil. A good imitation Castile soap consists of 65 per cent. olive oil and 35 per cent. tallow. The green colour is sometimes enhanced by adding chlorophyll compound.

Marine or Salt-water Soap is made from cocoa-nut oil, as described under "scouring soap" base. The cocoa-nut oil soap is a very firm one, which is easily soluble both in fresh and salt water, and yields a profuse lather. The soap must be free from filling of any kind, entirely soluble in salt water, *must not contain more than* 3 per cent. free sodium carbonate, 0.5 per cent. free caustic soda, 0.3 per cent. salt, 0.5 per cent. mineral matter (silicate of soda, sodium sulphate, etc.), 55 per cent. water.

Protein Soaps.—When protein matter—such as that contained in the germ of various cereals, oatmeal, rice gluten, etc.—is acted on by concentrated NaOH solution, the soap of amino-acids is produced which may be used as a substitute for marine soap, being said to leave no odour and to wash better in brine than marine soap. See English Patents, 17,999, 1905; 23,546, 1905; 5,620, 1909; 20,089, 1909.

Mottled Soap is made from ordinary settled soap of good quality by finishing thin, and adding insoluble colouring matter (venetian red, ultramarine blue, yellow ochre, copperas or ferrous sulphate) in the proportion 4-8 oz. to 100 lbs. of soap; the soap is well boiled up, and run into hot frames and crutched by hand until the temperature sinks to 60° C., when all danger of the mottling agent sinking to the bottom is passed. On slowly cooling, the soap crystallises out, and the pigment is expelled from the crystallising soap into portions which are still fluid, and this portion finally cooling, the foreign matter remains mixed with the softer or more fluid soap. To obtain a good mottle the soap must at first be very fluid, and must slowly cool in order that the crystallising should not be too rapid, otherwise only a discoloration or a very fine mottle results. Such mottled soap is usually made in small batches as it is difficult to incorporate the pigment evenly throughout a large mass of soap.

Settled Rosined Soap is made as described on p. 103, and is the one generally used for ordinary washing purposes, since the rosin imparts to the hard tallow soap softness and lathering power, besides being of considerable detergent value itself. For certain purposes, however, the presence of rosin in soap is very injurious.

Pure Rosin Soap, *i.e.*, sodium rosinate—prepared by dissolving colophony (ordinary rosin) in caustic soda—is used on a large scale for paper sizing (see Paper Making). It is described on p. 199 under **Paper Making.**

Potassium Soaps, Soft Soaps.—Soft soap is sometimes defined as soap made from low-melting point stock by use of caustic potash. Such soap is semi-transparent, soft, unctuous, and very soluble in water and deliquescent. It must be noted, however, that while *all* potassium soaps are soft, some sodium salts now manufactured are also quite soft (see p. 107).

Linseed oil, cotton-seed oil, corn oil, olive oil, olive-oil foots mixed with tallow, and tallow, are the stocks usually used.

A potash linseed-oil soap retains its transparency throughout summer and winter. Rosin may be used in very small proportions to increase its lathering and detergent qualities. Red oil forms a good, odourless potash soap; tallow produces a white potash soap.

The saponification is completed in the usual way, but without graining, and the soap is run through the crutcher directly into barrels and stored in a cool place. The glycerol is thus usually retained in the soap. Usually 100 lbs. of stock yield 225-250 lbs. of potash soap. About 30 lbs. of potassium chloride can be incorporated, giving a yield of 270-280 lbs. Higher yields than this are obtained by adding a binding agent, such as starch. Fillings of chlorides, carbonates, and silicates of potassium and sodium are used, the sodium salts, however, being less preferable. Soap powder has displaced these soaps.

Floating Soap is made by churning up a pure white settled and perfectly neutral soap (best made from tallow mixed with 25 per cent. cocoa-nut oil) in a special crutcher, the whole being heated about 80° C. The soap is beaten up into a froth and air incorporated with it to such an extent that the mass is lighter than water.

Shaving Soap is made from the best edible tallow by the grained process; it must be perfectly neutral. Cotton-seed and cocoa-nut oils are unsuitable as stock ingredients. The lye used for saponification usually consists of 25 per cent. KOH and 75 per cent. NaOH. The soap should contain very little water, and must be milled. During milling 8-10 per cent. of glycerol and 1 per cent. of tragacanth gum (which gives a permanent lather) are introduced.

Medicated Soap consists of ordinary soap mixed with small quantities of disinfecting or germicidal agents, such as phenol, cresol, etc. Almost invariably they are quite useless for the purpose for which they are intended, being scarcely more effective than a pure neutral soap, which itself has a considerable germicidal action, and is a valuable, although slow, disinfectant.

Formaline Soaps.—Liquid formaline soap consists of 10-25 per cent. formaline added to olive oil, alcohol, and essential oils. **Solid** formaline soap consists of 5 per cent. paraformaldehyde added to soap. Strong disinfectant.

Iso Soap is a solid sulphonic derivative of castor oil. Gives clear neutral solution, and forms, even with the hardest water, no insoluble lime salts. Hence is used for washing, dressing, bleaching, etc., in textile trades.

Filling Agents

A very great number of substances are incorporated into soap.

Rosin is a proper constituent of soap, the sodium salts of the rosin acids possessing valuable detergent properties.

Sodium Silicate and Borate also possess detergent properties, but are often used in such large quantities in the cheaper soaps as to almost be regarded as adulterants. Silicated soaps harden on ageing, the silicates imparting firmness to a soft inferior soap. Ultimately such soaps become stonelike as regards hardness.

The following is Dr Leed's scheme (*Chem. News*, xlviii. 67) for the complete analysis of soap :—

Weigh out 10 g. of sample. Dry at 110° C. Loss = water. Extract with petroleum ether.

Extract is uncombined fat. Dry at 110° C., and weigh.

Residue is soap and mineral constituents. Treat with alcohol.

Extract is *soap*, glycerol, and free alkali. Add 2-3 drops of phenolphthalein, titrate with $\frac{N}{10}$ H_2SO_4

Residue.—Na_2CO_3, NaCl, Na_2SO_4, sodium silicate, starch, and insoluble residue. Wash with 100 c.c. water.

$\frac{N}{10}$ H_2SO_4 used is due to *free caustic alkali*. Calculate as *NaOH*.

Add large excess of water, boil off alcohol, decompose with excess of $\frac{N}{1}$ H_2SO_4, boil, filter, wash.

Filtrate.—Na_2CO_3, NaCl, Na_2SO_4, sodium silicate. Divide into four equal parts.

Residue.—Starch and insoluble residue. Dry, filter, and weigh; the weight is the starch and insoluble residue starch. Convert into $C_6H_{12}O_6$, titrate with Fehling's solution, subtract the weight of *starch* found. The difference is the insoluble mineral constituents.

Filtrate. Combined soda and glycerol. Titrate excess of acid back with $\frac{N}{10}$ NaOH.

Residue, fatty acids and rosin. Dry at 110° C. *Estimate the rosin*. Subtract this. Difference = fatty acids.

Na_2CO_3. Titrate with $\frac{N}{10}$ H_2SO_4, and calculate as Na_2CO_3.

NaCl. Titrate with $\frac{N}{10}$ $AgNO_3$, calculate as NaCl.

Na_2SO_4. Precipitate with $BaCl_2$, weigh the $BaSO_4$, calculate as Na_2SO_4.

Sodium Silicate. Decompose with HCl, and determine soda combined in silicate and silica.

$\frac{N}{1}$ H_2SO_4 used up is due to *combined* Na_2O in soap.

After titration evaporate dry on water bath. Extract with absolute alcohol, evaporate the filtered solution in a weighed flask. Weigh any *glycerol*.

Express Results thus—

	Per cent.
Fatty acids	.....
Rosin	.....
Soda (existing as soap)	.....
Water	.....

	Per cent.
Sodium carbonate	.....
,, hydrate	.....
,, chloride	.....
,, sulphide	.....

	Per cent.
Silica	.....
Soda in sodium silicate	.....
Lime	.....

Petroleum Naphtha, to the extent of 10 per cent., is sometimes incorporated in soap in order to increase its detergent action. The petroleum is mixed with a rosin soap mass, and the mixture added to the common soap.

Colouring Matters and perfumes (ethereal oils) are added, either to disguise inferior and evil-smelling and discoloured soap, or to please intending buyers.

Scouring Soaps often contain sand, kieselguhr, powdered pumice, etc. Some soaps contain sulphur, flour, talc, china clay, salt, etc. etc.

Persulphates, Percarbonates, and Perborates have been added to soaps in order to give them bleaching and disinfecting properties (see Peroxide Soaps, p. 115).

Statistics.—The following numbers show the amount of soap **exported** by the United Kingdom in 1910:—

	Cwt.	Value.
Soft soap	32,116	£24,487
Household and laundry soap in bars or tablets	1,345,598	1,357,776
Polishing and scouring soap	9,867	16,070
Soap powder	26,478	30,790
Toilet soap	74,145	357,781
Other sorts (including cotton-seed oil soap)	4,259	10,639
Total of soap	1,492,463	£1,797,543

The value of the imported soap in 1910 (principally household or laundry) was £454,000. The greater part of the soap produced in the United Kingdom is consumed at home.

The United States in 1910 *imported* 3,928,000 lbs. (value, 499,000 dols.) of toilet and fancy soap, and $247,000 worth of other varieties. The *export* in the same year was:—*Toilet or fancy soap, value,* $1,480,000. *Other kinds,* 45,716,000 lbs. *Value,* $2,141,000.

ANALYSIS OF SOAP

Rosin.—To detect rosin, dissolve some of the fatty acids above separated in warm acetic anhydride, *cool,* run in slowly sulphuric acid of sp. gr. 1.53 (made by mixing 34.7 c.c. concentrated H_2SO_4 with 37.5 c.c. water, and cooling). A fugitive violet colour indicates rosin. Cholesterol gives same reaction, and should be removed in original soap before liberating the fatty acids by shaking out with ether.

To *estimate* rosin, weigh 2-3 g. of liberated and dried fatty acids into a flask, dissolve in ten times their volume *absolute* alcohol (not 90 per cent. alcohol), cool flask in cold water and drive for forty-five minutes a current of *dry* HCl gas through the liquid, stand for one hour, dilute with five times the volume of water, boil till clear, extract thoroughly in a separating funnel with ether, separate ethereal extract which contains the rosin, wash with water until all HCl is removed from it (test wash water with $AgNO_3$), add 50 c.c. alcohol, and titrate with standard NaOH, using phenolphthalein as indicator. Each c.c. of $\frac{N}{1}$ NaOH used up corresponds to 0.346 g. rosin.

Glycerol.—For detection and estimation, see **Glycerol.**

Sugar is sometimes present to 25 per cent. in cheap transparent soap. Estimate in usual way with Fehling's solution, diluting to avoid oxidation of glycerol. If much glycerol is present add slaked lime to combine with the sugar, add same amount of washed and recently ignited sand, boil down to a syrup, cool, pulverise, exhaust in a corked flask with 80-100 c.c. of alcohol-ether mixture (in equal volumes). The solution contains the glycerol (free from sugar), which is estimated by evaporating in usual way.

Starch is detected by a microscopical examination of residue insoluble in alcohol. Confirm by iodine test. For estimation see Starch.

Dextrine contained in the water solution with the sugar is estimated by precipitating with alcohol, stirring vigorously with a glass rod in a weighed beaker, pouring off the aqueous liquor, washing residue with alcohol, drying at 100° C., and weighing.

Gelatine is detected by washing the alcohol-ether insoluble residue with hot water, and testing filtrate with tannic acid.

TABLE OF ANALYSIS OF VARIOUS SOAPS (*Hope*)

Description of Soap.	Origin.	Fatty and Rosin Anhydrides.	Soda, Na_2O, existing as Soap.	Silica.	Soda as Silicate.	Caustic and Carbonate of Soda.	Sodic Chloride.	Sodic Sulphate.	Lime, Oxide of Iron, etc.	Water.	Total.	Fatty and Rosin Acids.
White, No. 1	Tallow	69.06	8.98	0.01	*nil*	0.27	0.49	0.16	0.07	21.14	100.18	71.20
,, ,, 2	Tallow and cocoa-nut-oil	60.50	6.82	0.06	,,	0.06	0.11	0.12	0.16	32.20	100.03	62.36
,, ,, 3	,, ,,	55.71	6.90	0.03	,,	0.92	0.18	trace	0.08	36.54	100.36	57.44
,, ,, 4	,, ,,	44.27	6.23	7.02	2.36	0.75	0.32	0.34	0.34	38.14	99.77	45.64
Cold water, No. 1	Tallow, rosin, and cotton-seed oil	71.30	7.98	1.07	0.48	0.75	0.36	0.30	0.16	17.44	99.84	73.50
,, ,, 2	,, ,,	49.95	7.00	2.34	1.01	0.33	0.51	*nil*	0.50	38.18	99.82	51.50
Olive oil, No. 1	Olive oil	71.20	7.58	0.06	0.03	0.22	0.66	0.17	0.20	19.70	99.82	73.40
Marseilles, No. 1	Chiefly olive oil	62.66	7.27	0.06	0.03	0.77	0.76	0.30	0.16	28.20	100.21	64.60
Palm oil, No. 1	Palm oil	59.28	6.65	0.42	0.01	0.39	0.47	0.13	0.16	32.35	99.86	61.08
Mottled	Palm-nut oil	38.89	5.76	6.40	1.29	1.62	1.78	0.72	0.03	38.70	95.19	40.10
Satinet	Tallow and rosin	59.92	6.76	0.02	*nil*	0.92	0.41	0.37	0.05	31.30	99.75	61.77
Glasgow almond	,, ,,	42.41	4.14	5.64	1.59	2.76	0.37	trace	0.14	42.88	99.93	43.72
Pale rosin, No. 1	,, ,,	60.90	7.22	0.04	*nil*	0.10	0.46	0.12	0.02	31.22	100.08	62.78
,, ,, 2	,, ,,	48.20	5.00	0.42	0.18	0.15	0.65	0.10	0.10	45.00	99.80	49.65
,, ,, 3	,, ,,	39.92	4.70	0.62	0.25	0.20	1.48	0.18	0.15	52.40	99.90	41.15
Milling	...	63.06	7.25	0.02	*nil*	0.10	1.65	0.15	0.30	27.47	100.00	64.95
Yellow (for foreign markets)	...	10.90	1.36	0.03	,,	trace	2.57	0.56	0.14	84.00	99.56	11.20
Marine (for emigrants)	Palm-nut oil	19.42	3.11	9.00	3.98	3.00	5.13	0.35	0.16	53.32	97.47	20.02

Phenol or Cresol in soap is roughly estimated by dissolving 100 g. of soap in hot water, making alkaline with NaOH, precipitating soap with salt, filtering off soap and washing it on filter with saturated brine, boiling down the brine solution, precipitating any dissolved soap again with brine, filtering, boiling filtrate to small bulk, transferring solution to a 50 c.c. stoppered graduated cylinder, adding salt so that some remains undissolved, acidifying with sulphuric acid, and reading off the volume of separated phenols, each c.c. representing 1 g. of phenol. For greater accuracy dissolve the phenols in ether, distil off ether, and estimate by *Koppeshaar's method.*

For further details the reader should consult one of the larger treatises on soap, or Allen's "Commercial Organic Analysis."

Acknowledgments. — The author has pleasure in thanking Mr W. H. Stephens, A.R.C.S., for expert advice regarding the newer processes employed in the soap industry.

XI.—GLYCEROL OR GLYCERIN*.

By G. Martin, Ph.D., M.Sc.

LITERATURE

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METHODS OF OBTAINING GLYCEROL FROM WASTE SOAP LYES

The waste lye as discharged from the soap kettle should contain 4-8 per cent. of glycerol, and be nearly neutral (0.04-0.4 per cent. NaOH are limits of alkalimetry), otherwise much valuable acid will be wasted in neutralising the excess of alkali. The greater the inferiority of the stock used in the manufacture of soap the greater will be cost of recovery of the glycerol present in the lye, both on account of the great amount of foreign organic matter present in the lye, which must be removed, and also because of the smaller amount of glycerol present in the stock.

Two systems are at present in vogue for glycerol recovery, namely:—

1. Van Ruymbeke's Process.
2. Garrigue's Process.

We will discuss each in turn.

Van Ruymbeke's Process of Glycerol Recovery

The waste lye reduced to its lowest practicable degree of alkalimetry, viz., under 0 4 per cent. NaOH, is run from the soap kettle to the storage tanks to cool; here any dissolved soap separates and heavy impurities sink to the bottom. The liquor is then run into the treating tank A (Fig. 41), made of sheet steel and provided with open steam pipes at the bottom for heating, and an air-jet for mechanical agitation. If the waste lye is strongly alkaline, either sulphuric or hydrochloric acid is run in until the liquor is almost neutral, and then basic ferric

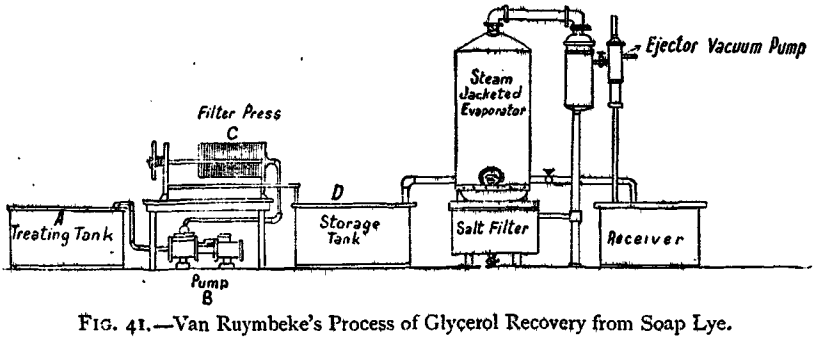

Fig. 41.—Van Ruymbeke's Process of Glycerol Recovery from Soap Lye.

* The pure chemical product is termed "Glycerol" (which shows that it is an alcohol) while the impure commercial product is called "Glycerin." Since this introduces an entirely superfluous complexity we will throughout the article use only the scientifically correct term, viz., glycerol.

sulphate solution added in the proper proportions. If, however, the liquid is only slightly alkaline the iron salt alone is used for neutralisation. Usually three-fourths of the alkali are neutralised by acid, and the remainder by the basic iron sulphate.

The iron salt is known as "Chemical sand," and is made by mixing a finely powdered and dried iron ore (analysing 50 per cent. iron oxide) with concentrated sulphuric acid (60° Be.) previously heated to 150° C. The mass is then run on to an iron floor, where the reaction continues and the mass solidifies. It is then broken up and heated for some hours at 200°-280° C. It then forms a mixture of ferric sulphate, ferric oxide, and a little free acid. Instead of this iron salt any of the alums may be used as a precipitant. They are, however, somewhat more expensive.

The acid added to the soap lye decomposes any soap present, setting free the fatty acids. The iron salt then precipitates these acids as insoluble iron soaps, and at the same time carries down any albuminous matter (coagulated by heat).

The lye is then forced by means of the pump B through the filter press C, which retains the precipitated impurities, the lye flowing into another similar tank (not shown) where the process of purification is completed. The lye is then filtered off into the third tank D. It should now be clear, and possess a slight acid reaction. The exact amount of dry soda-ash to neutralise the liquor is now thrown in and thoroughly mixed, and the lye filtered from the resulting precipitate. It is then ready for evaporation in a "vacuum evaporator." This consists of a sheet-iron boiler heated internally by a series of steam pipes, while a vacuum pump maintains inside the vessel a vacuum of between 18 and 28 in. Under the diminished pressure the water boils off rapidly leaving the glycerol behind. In order to increase the effect sometimes two or three of these evaporators are used in series ("double" or "triple" effect), the vapours from the first being used to heat the liquid in the second, and those of the second to vaporise the liquid in the third. In this way a greatly increased evaporative effect is obtained with the same amount of steam. As the liquid concentrates salt is deposited. It falls between the heating pipes of the boiler, and collects at the bottom, whence it is from time to time withdrawn through doors placed at the bottom of the vacuum chamber.

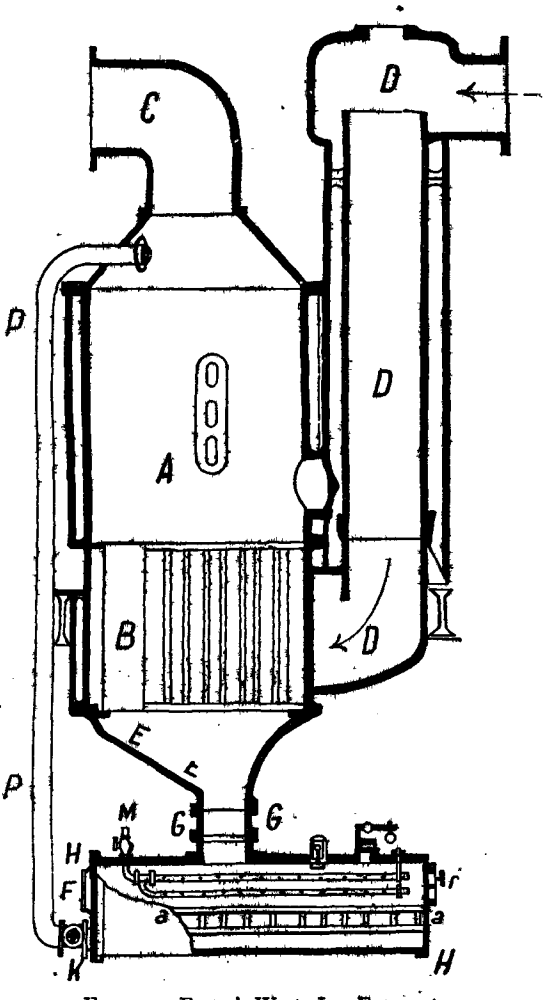

FIG. 42.—Foster's Waste Lye Evaporator.

Fig. 42 shows a section of Foster's Waste Lye Evaporator.

The lye is boiled in the vessel A by means of the steam pipes B, the vapours rising up through which is connected with the vacuum pump. If the vessel is employed in multiple effect the hot

vapours from the other vaporisers pass into the liquid by DDD, and help to maintain the evaporation, since the vacuum is greater in the second boiler than in the first, and so the vapours from the first boiler passing into the second are hot enough to maintain the liquid in it in rapid ebullition. The salt is deposited on the sloping hearth EE, and finds its way into the salt filter HH, the salt resting on a filter bed *aa* of iron netting and copper gauze placed over the gridiron plate. When the filter is filled with salt (which can be seen through the sight glass F) the valve at G is shut so that communication between the salt in HH and the vacuum in A is cut off; then the valve K is opened to the vacuum space in A, and a stream of steam is driven through M into the closed chamber, and drives the liquid through the salt in HH, the liquid and steam being sucked through PP into the top chamber A, leaving the salt on the filter *aa* quite dry. Then K is closed and the salt removed through a door *r*. The operations are therefore continuous, the salt being removed from time to time without breaking the vacuum. Usually two filter chambers are fitted to each evaporator, matters being so arranged that one is open to receive salt at the same time that salt is being removed from the other, so that a practically continuous withdrawal of salt takes place. Many other systems of evaporators (*e.g.*, Jobbins) are in use, all of which offer some special advantage. The salt separated is again used in soap graining.

The loss of glycerol by evaporation is extremely small when the operation is carried out under a vacuum of 26 in. and with steam at a low pressure. The liquid is boiled until a sample of lye withdrawn shows a density of 30° Be. at 15° C., when it consists of 50 per cent. glycerol, while most of the salt has been deposited and withdrawn. Then the liquid is sucked into a storage tank situated below the evaporator, allowed to cool, separated by filtration from any precipitated salt, passed into a second evaporator of a similar type but smaller, and the evaporation carried on until the proportion of glycerol reaches 80 per cent., the salts and water varying between 10 per cent. and 12 per cent. This glycerol is known as "Crude" and is now distilled.

Distillation of Crude Glycerol.—The still A (Fig. 43) consists of a steel boiler maintained at a high vacuum of 28 in. while its contents are heated by dry steam at 150° C. circulating through closed steam coil *aa*, while at the same time a current of live steam at 150° C. is blown through the glycerol by means of an open jet *bb*. This steam enters at *c*, passes down the tube *cde*, and suddenly expands to twenty or thirty times its original volume from the narrow tube *ef* into the wide steam coil *ggg*, which is placed in the steam heated chamber BB (felt-covered to avoid loss of heat) and which is filled with steam at 150° C. The steam in expanding from *ef*

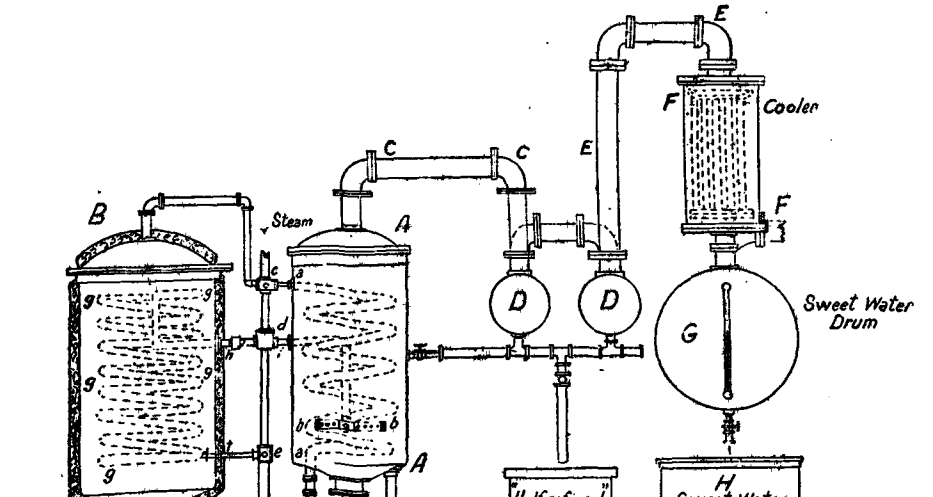

FIG. 43.—Jobbins Glycerol Distilling Apparatus.

into the wide coil *gg* has its temperature lowered, but the free steam at 150° C. in the superheater BB heats the expanded steam in the coil *gg* to its original temperature again, and this steam, in its expanded and dry condition, rushes through the pipe *hi* and blows in a dry hot stream through the jet *bb* into the glycerol in AA and causes it to distil rapidly, owing to the high vacuum maintained in AA, up through the pipe CC, into the drums DD, where practically pure glycerol collects ("half-refined"), while steam and the more volatile products pass away up the pipe EE through a series of pipes placed in a cooler FF, through which cold water circulates. Here the glycerol and steam are completely condensed and flow into the drum G, whence it is drawn off from time to time into the tank H. This latter distillate is known as "sweet-water" and contains a small amount of glycerol and volatile organic acids. It is worked up again for pure glycerol.

The level of the glycerol in the still AA is maintained constant during the distillation, liquid being continually admitted slowly to maintain the level constant as the liquid distils away. Finally there remains in A a considerable quantity of "glycerol foots," containing 30·50 per cent. of glycerol, which is recovered from it by a special process described below.

The "half-refined" glycerol which collects in DD is distilled once again and thus obtained pure.

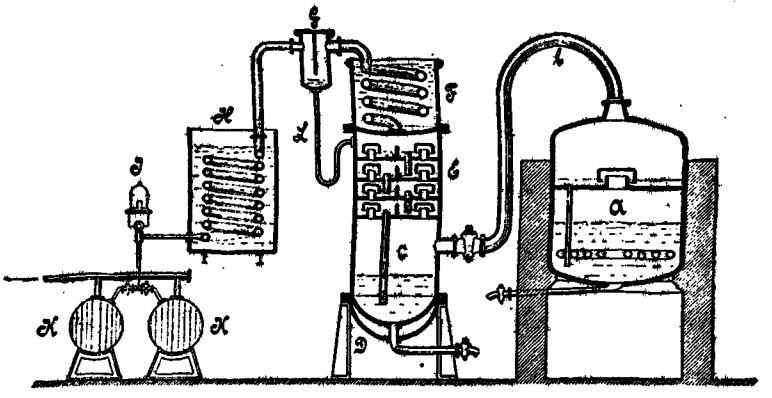

FIG. 44.—Heckmann's Glycerol Distilling Plant.

Fig. 44 shows a glycerol distilling plant designed by Heckmann, and much used in Germany. Glycerol is boiled in *a* by indirect steam, a high vacuum being maintained by a pump attached to KK, which lowers the boiling point of the liquid in A to about 200° C. The glycerol vapours and steam pass away through G into the rectifying column CE, to which is attached the *dephlegmator* F. The liquid condensing in C is maintained at about 80° C. by means of the steam-jacketed bottom D, so that the water scarcely condenses at all in this part of the apparatus, but passes away as steam, mixed with glycerol vapours, through the bell condensing trays in E, into the dephlegmator F, and finally reaches the catch-all G, where any condensed glycerol runs back through L into C, and is again distilled there. Consequently only concentrated glycerol collects in C, while steam and a very small amount of glycerol vapours pass over from G into the condenser H, the specific gravity of the water condensing in H being checked by a swimming hydrometer contained under a glass bell jar J. The glycerol in C is then withdrawn and decolourised with blood or animal charcoal (which has been carefully freed from mineral matter by extracting for weeks with HCl and washing with water).

Concentration and Distillation of Sweet-Water.—The sweet-water contains volatile organic acids, either free or combined with glycerol. It is therefore mixed with the exact amount of soda-ash to retain such acids in the "foots" as alkali salts. Next, the sweet-water is placed in the steel boiler AA, Fig. 45, provided with a steam heating coil *aa*; *cd* is a plate provided with a hole, at a short distance below which is another circular plate *ef* of slightly larger size, which prevents the liquid splashing up the tube BB, and consequently is known as the "dash plate." The valve *h* is closed, and a high vacuum is maintained in the concentrator AA by means of a vacuum pump connected with the receiving drum D. The liquid boils,

water vapour passes over through BB, and entering the catch-all CC, impinges against the tube *kl*, deposits the less volatile glycerol in the catch-all, while the water vapour, passing on, enters the tube *kl* and is deposited in the drum D. The glycerol deposited in CC is run back from time to time by means of *mn* into the concentrator AA.

When the glycerol in AA is sufficiently concentrated it is run into a Jobbins' distilling plant, previously described, and preferably made of tinned copper, and there finally distilled. It is finally concentrated to the proper specific gravity (1,262) and sold as "dynamite glycerol."

Refined glycerol is usually clarified by mixing a small quantity of bone-black with the hot liquid, and filtering. The product is of straw colour and is known as "dynamite glycerol." Colourless water-white glycerol is produced by a subsequent distillation and clarification of the dynamite refined grade.

Utilisation of Glycerol Foots.—The "foots" comprise the tarry residue left in the still in the distilling process. They contain from 30-50 per cent. of glycerol, 5 per cent. of salt, 20-30 per cent. of sodium acetate, and 10-15 per cent. of sodium salts of non-volatile fatty acids. The glycerol is removed by acidifying the mass with the exact amount of sulphuric acid necessary to combine with the sodium present—the sodium being estimated in a sample by incinerating and weighing as sodium

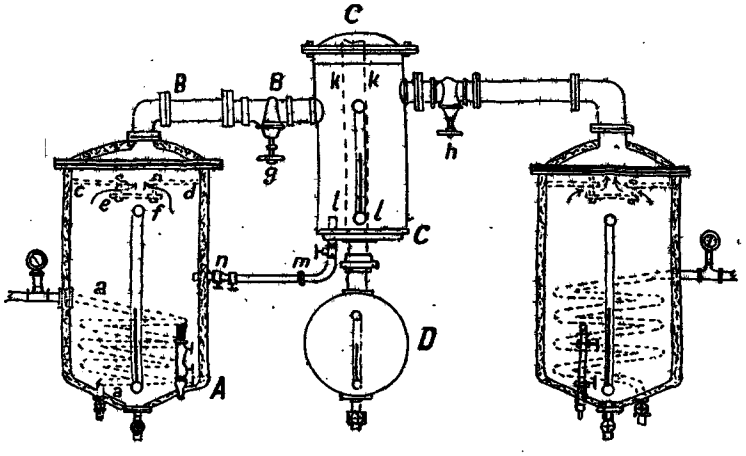

FIG. 45.—Plant for Concentrating Sweet-Water.

carbonate—in a lead-lined tank, and the darkened mass is, after standing, run through coarse filter bags and heated in an iron still, when the organic acids (principally acetic) volatilise. Finally the product is added to the waste lye direct from the soap kettle and worked up along with this for glycerol.

Garrigue's Process for Glycerol Recovery

This method presents the following advantages over van Ruymbeke's process:—

1. In van Ruymbeke's system the volatile fatty acids (*e.g.*, acetic, butyric, caprylic, etc.) are imperfectly eliminated, distilling over with the glycerol even from an alkaline solution, and injuriously affecting the quality of the refined product. In Garrigue's system the volatile fatty acids are almost entirely eliminated *before distilling*.

2. In van Ruymbeke's system the presence of much alkali in the liquor to be distilled (added to the sweet-water in order to fix the fatty acids) greatly retards the distillation and does not effect complete separation, since some of the volatile fatty acids distil over with the glycerol, while some glycerol remains behind in the foots. In Garrigue's system so small an amount of alkali is used that it scarcely effects the distillation.

3. In van Ruymbeke's system considerable amounts of glycerol foots occur as residues in the still. These contain sometimes over 50 per cent. glycerol and cannot be economically discarded; the glycerol has therefore to be recovered by mixing with sulphuric acid as described above, and mixing the product with the raw material. Since the foots contain sodium salts of organic acids, these contaminate the glycerol. In Garrigue's system the foots produced are so small in quantity and so poor in glycerol that they can be discarded.

Details of Garrigue's Process of Glycerol Recovery.—The soap lye from the soap kettle is run into a storage tank, where any soap separates out and heavy impurities subside. Next it is run into the treating tank A, and there is added about 0.5 per cent. of aluminium sulphate (or common alum) and sufficient sulphuric acid to nearly neutralise the caustic soda and sodium carbonate present. The contents of the tank are agitated by means of air blown in from a Korting's exhauster B through a perforated coil in the bottom of the tank. The sulphuric acid sets free the insoluble fatty acids before in the solution as soap, while the aluminium present at once precipitates them as insoluble aluminium soaps. After sufficient agitation, the liquid is forced by the pump C through the filter press D into the feeding tank E. The liquid is now clear. It then passes to the vacuum evaporator F and is concentrated (the level in the evaporator being kept constant by a continual introduction of lye in proportion as the liquid boils away). The concentration is carried on until the residual liquid contains about 40 per cent. of glycerol, and about 80 per cent. of the chloride and sulphate of sodium originally present in the liquor have crystallised out and been recovered in the usual way.

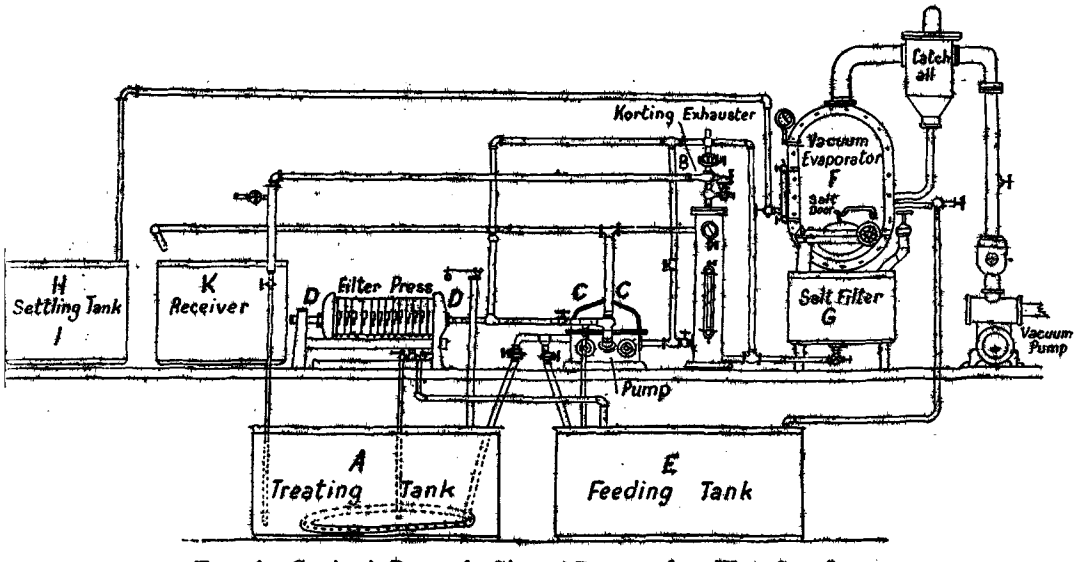

FIG. 46.—Garrigue's Process for Glycerol Recovery from Waste Soap Lye.

Next the liquid is allowed to flow from the evaporator F through the salt filter G (using a vacuum of 20 in. beneath the salt filter to force the liquid through), and is pumped away to the settling tank H.

So far the soluble and volatile fatty acids have remained in solution; these are now removed as follows. The concentrated liquor is pumped from the settling tank H into the treating tank A, and about 0.5 per cent. barium chloride, $BaCl_2$, stirred in. All the sodium sulphate remaining in the liquor is precipitated as barium sulphate, while any soap still present is decomposed and precipitated as an insoluble barium soap. Now sufficient sulphuric acid is added, sufficient to decompose all the alkali compounds of the volatile and soluble fatty acids, whereby the latter are set free, and in turn are almost completely precipitated as insoluble barium compounds, with the excess of barium chloride remaining in the liquid; thus the volatile acids are removed.

The amount of sulphuric acid required is estimated by withdrawing a sample of liquor, filtering it, weighing off 10 g. into a flask, adding 140 c.c. of distilled water, and 1 c.c. of concentrated sulphuric acid, connecting the flask with a Liebig's condenser, and distilling over 100 c.c. Finally,

this volume, which contains all the volatile acids, is titrated with standard caustic soda solution, using phenolphthalein as indicator. The organic acidity is then calculated in terms of sulphuric acid, and then the necessary charge of sulphuric acid for the total amount of crude liquor is calculated and run in.

After a thorough agitation the liquid is filtered through the filter press D, Fig. 46, into the feeding tank E, and is thence pumped into the evaporator F, and concentrated until the level of the liquor in the gauge glass remains constant. The volatile fatty acids still remaining (for they are not completely precipitated by the barium chloride) are in part expelled with the water vapour, but part remains to combine with the glycerol as the concentration proceeds, and are retained by it in the form of glycerides. Finally, when the concentration has proceeded so far that the liquid contains 85 per cent. of glycerol, it is discharged from the evaporator F into the receiver K, and is tested for total acidity by adding excess of standard alkali to a measured sample of the hot glycerol, heating, and titrating back the excess of alkali with standard sulphuric acid. This gives the measure of organic acids still present. The amount of a saturated solution of sodium carbonate (soda-ash) required for neutralisation is now calculated, and added to the crude glycerol in the receiver K, the amount being sufficient to render the mass slightly alkaline. The crude glycerol is now distilled.

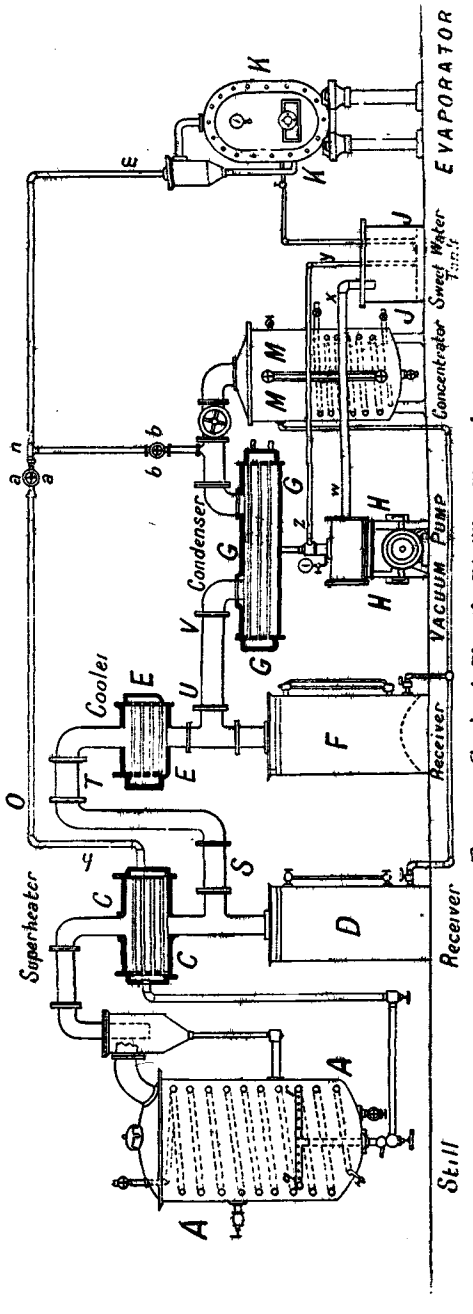

FIG. 47.—Garrigue's Plant for Distilling Glycerol.

Garrigue's Process for Distilling Glycerol.—Fig. 47 shows a complete Garrigue's plant for glycerol distillation. A is the still in which the crude glycerol is heated to about 163° C. by a closed steam coil, while a vacuum pump H maintains a vacuum of about 28 in. Under these circumstances the glycerol rapidly distils. K is an evaporator, filled with "sweet-water" from a previous distillation. This glycerol water is heated by closed steam coils in the evaporator (the steam used is low pressure direct from the exhaust of the vacuum pump H), while a vacuum of about 22 in. is maintained within the vessel. Under these circumstances the

glycerol water rapidly boils, and a current of steam at a temperature considerably below 100° C. is driven along the pipe *mnoh*, and rushes through a series of tubes running through the centre of a chamber C (the "superheater"), which is filled with hot glycerol vapours at about 160° C. on their way from the still A to the receiver D. Here a double action occurs. On the one hand the cooler pipes conveying the steam from K serve to condense the glycerol, while on the other hand the hotter glycerol vapours serve to heat the pipes, and consequently the sweet-water vapours become greatly superheated to a temperature of about 160° C., and blow rapidly in this dry superheated condition through the perforated coil *qr* into the boiling glycerol in the still, and aids its distillation. The abstraction of heat from the vapour of the distilling glycerol where it meets the steam pipes in C causes a large part of the glycerol to condense on the tubes of the superheater, and thence drop into the first receiver D. This glycerol is a finished product, being almost water-white, with a density of 1.263. A large proportion of the glycerol vapours, however, pass on up the tube *st*, and enter a chamber E, called the "Glycerol Cooler." Through this chamber run a number of tubes conveying hot water, which, entering at a temperature of about 66° C., and leaving at about 88° C. (being heated in its passage by the hot glycerol vapours condensing on the tubes), causes the glycerol alone to condense and drop into the receiver F, while the steam passes on into the condenser G.

The glycerol condensed in F has a sp. gr. of about 1.250. It is not advisable for all the glycerol to condense in F, otherwise the volatile fatty acids which have escaped elimination in the crude glycerol evaporator would also condense and impart to the glycerol in F a too high acidity. Consequently matters are so arranged that about 3 per cent. of the total glycerol passes on with the steam through UV, and enters the sweet-water condenser GG. Here it enters a chamber filled with copper pipes carrying a stream of cold water, and consequently almost all the steam and glycerol condense to sweet-water, which, pouring down through the vacuum pump H, are passed by the tube *wx* into the sweet-water tank *JJ*.

Usually the sweet-water does not condense in quantity sufficient to keep the pump H properly sealed, and so it is usual to have a small return pipe *yz* from the open sweet-water tank to the pump suction, so as to allow some of the sweet-water to maintain a continuous circuit through the pump.

In the best practice matters are arranged so that about 2 lbs. of steam are injected into the still for every pound of glycerol distilled. Since the sweet-water should contain about 3 per cent. of the total glycerol, it follows that it should have a glycerol content of about 1½ per cent.

From the sweet-water tank J the sweet-water is fed continuously (being sucked in by means of the vacuum) into the evaporator K. The glycerol content of the sweet-water in K continually increases as the distillation proceeds, and at the same time there is a continual increase in the volume of sweet-water in circulation. When the glycerol in the evaporator K reaches about 25 per cent., it is run into the concentrator MM, and evaporated until the concentration becomes 80 per cent. glycerol. Since all the volatile acids gradually accumulate in the sweet-water, this concentrated glycerol must be returned to the still for redistillation. Towards the close of the operation the still A is shut off by closing the valve *aa*; the valve *bb* is opened, and the glycerol in KK is concentrated until it reaches 80 per cent. The aqueous vapours condensed from this concentration are run to waste through the vacuum pump.

In some works the contents of the sweet-water concentrator K are emptied from time to time into the settling tank of the crude glycerol plant, and fed with the rest of the glycerol into the still as required for distillation.•

While distilling it is best to maintain the feed of crude glycerol at a constant level, just above the perforated jet-pipes, during the whole time of distilling (twenty-four hours). The charge then left in the still is run into the waste lye treatment tank, where the colouring matter is removed by chemical means as previously described.

Uses of Glycerol.—By far the greater part of glycerol is used for making nitroglycerine; besides this it is used as a sweet conserving fluid for preserved

fruit, as a lotion or basis for ointments, in gas meters and hydraulic jacks to prevent freezing, for lubricating moulds, for preventing shrinkage in wooden vessels, in clay modelling, in artists' colours, in calico printing, in cements and inks, in photography, to impart elasticity to leather and paper, etc. Glycerol is sometimes (illegally) added to alcoholic drinks as an unfermentable and harmless sweetener.

Properties of Glycerol.—When pure, it is a solid, M.P. 20° C., but as usually obtained it is a sweet tasting, thick liquid, colourless, of sp. gr. 1.265 at 15° C., and B.P. 290° at 760 mm. (with slight decomposition), 210° C. at 50 mm., 179.5° C. at 12.5 mm., 163° C. at 10 mm. It does not volatilise at ordinary temperatures, but when heated at 100° C. a slight loss occurs, especially in the presence of steam. Heated with dehydrating agents it changes into acrolein, thus—

$$C_3H_8O_3 = C_3H_4O + 2H_2O.$$

When pure, glycerol ignites at 150° C., and burns gently with a pale blue flame without odour or residue.

Dynamite glycerol must have a minimum sp. gr. of 1.262, contain no CaO, H_2SO_4, or Cl, not more than 0.1 per cent. of ash, and must not reduce $AgNO_3$ solution. Glycerol derived from decomposing fats frequently contains trimethylene glycol, $C_3H_6(OH)_2$, which lowers the boiling point and specific gravity.

At 160° C. glycerol dissolves two-thirds of its weight of boric acid, forming glyceryl borate, $C_3H_5BO_3$, which is used as a preservative ("boro-glyceride"). Glycerol is miscible in all proportions in water and alcohol, sparingly soluble in ether (1,000 parts ether dissolve 2½ glycerol) and in ethyl acetate, 100 parts of which dissolve 9 of glycerol; glycerol is insoluble in chloroform, petroleum ether, benzene, and carbon disulphide, also in oils and fats. Glycerol is an excellent solvent, many substances dissolving in it with greater ease than in water or alcohol; thus it dissolves 98 per cent. soda crystals, 60 per cent. borax, 50.5 per cent. potassium arsenate, 50 per cent. zinc chloride, 40 per cent. alum, 40 per cent. potassium iodide, 30 per cent. copper sulphate, 25 per cent. ferrous sulphate, 25 per cent. potassium bromide, 20 per cent. lead acetate, 20 per cent. ammonium carbonate, 20 per cent. arsenious oxide, 20 per cent. arsenic acid, 20 per cent. ammonium chloride, 15 per cent. oxalic acid, 10 per cent. barium chloride, 10 per cent. copper acetate, 8 per cent. sodium bicarbonate, 7.5 per cent. mercury bichloride, 5 per cent. calcium sulphite, 3.5 per cent. potassium chlorate, 1.9 per cent. iodine, 1 per cent. calcium sulphate, 0.7 per cent. iron oleate, 0.9 per cent. magnesium oleate, 1.18 per cent. calcium oleate. Glycerol also dissolves caustic alkalis, alkaline earths, and lead oxide, and in the presence of caustic alkalis also ferric oxide, cupric oxide, and bismuth oxide.

Glyceryl Phosphoric Acid, $C_3H_5.(OH)_2.O.PO(OH)_2$.—Formed by mixing P_2O_5 with glycerol, and known only in aqueous solution (20-50 per cent.). Dibasic acid. Salts used medicinally, having a strong action on the nervous system. In this form phosphorus is rapidly assimilated. **Tonal** is the name given to preparations of its salts, **kalio-tonal** being potassium glyceryl phosphate.

Statistics.—The world's production of glycerol amounts to 80,000 tons. *Germany* produces about 10,000 tons. England imported in 1910 about 4,000 tons, of value £230,000; she exported 11,900 tons, of value £653,000. The United States imported in 1910 41,182,000 lbs., of value $3,666,000.

Detection and Estimation of Glycerol.—To detect glycerol dry the substance thoroughly at 100° C., mix with twice its weight of finely powdered potassium hydrogen sulphate, and heat (on the sand bath) in a small flask fitted with a leading tube passing into a test-tube placed in a freezing mixture. In the presence of glycerol the characteristically smelling acrolein will be evolved, the presence of which may be confirmed by adding to the liquid in the test-tube a few drops of a mixture of 3 g. of silver nitrate in 30 g. ammonia (sp. gr. 0.923), and 3 g. of sodium hydroxide in 30 g. water. A silver mirror should rapidly appear.

Estimation of Glycerol in Fats.—The glycerol is separated from the fat by saponifying with alcoholic KOH, filtering the soap solution, setting free the fatty acids by HCl, and filtering them off. The aqueous extract, containing all the glycerol, is neutralised with $BaCO_3$, evaporated, and the glycerol extracted with ether. On evaporating the ether the crude glycerol is left and may be weighed. A weighed portion of this glycerol is acetylated in the usual way with acetic anhydride and dried sodium acetate, the excess of acetic acid *exactly* neutralised with NaOH in the cold, and the number of acetyl groups in the $C_3H_5(OC_2H_3O)_3$ determined by adding *excess* of standard NaOH, and boiling and titrating back with acid. From the equation—

$$C_3H_5(OC_2H_3O)_3 + 3NaOH = C_3H_5(OH)_3 + 3C_2H_3O_2Na,$$

it will be seen that 3 molecules of NaOH used up denote 1 molecule of glycerol present. The amount of glycerol in the whole may then be estimated. This method cannot be used for waste soap lye and other products low in glycerol. It gives somewhat low results.

Estimation of Glycerol in Soap Lyes.—250 c.c. of soap lye is acidified with H_2SO_4, the fatty acids filtered off, lead acetate added, the precipitate filtered off, the solution evaporated, made up to 100 c.c., and 25 c.c. are boiled thirty seconds with 25 c.c. concentrated H_2SO_4 and 40 c.c. $K_2Cr_2O_7$ solution containing 75 g. per litre. From the equation—

$$3C_3H_8O_3 + 7K_2Cr_2O_7 + 28H_2SO_4 = 9CO_2 + 40H_2O + 7Cr_2(SO_4)_3 + 7K_2SO_4,$$

it will be seen that for every 1 g. of glycerol oxidised 7.5 g. of dichromate disappear. The exact strength of dichromate before and after boiling is found by titrating with ferrous ammonium sulphate in the ordinary way. From the loss in strength of the dichromate the amount of glycerol can be calculated. The results are usually too high.

For a critical survey of other methods of glycerol estimation the reader is referred to Allen's "Commercial Organic Analysis," Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats, and Waxes," or Wright-Mitchell's "Oils, Fats, and Waxes."

XII.—ESSENTIAL OILS

By C. Ainsworth Mitchell, B.A., F.I.C

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The volatile essential oils, which are produced in numerous plants, differ from the fixed oils in many important particulars.

Most essential oils are mobile odoriferous liquids which, as a rule, may be distilled without undergoing decomposition, and usually they are composed of several constituents, in one or more of which the characteristic aroma of the oil is concentrated.

In some plants the essential oil is contained in the blossoms, while the rest of the plant contains little or none. In other plants, such as those that produce spices, the bulk of the oil may be in the root or bark; whilst in others, again, essential oil, in proportions varying with the stage of growth, occurs in all the organs of the plant.

Various methods of separating the oil are in use, the choice depending upon the nature of the oil and the quantity that can be extracted.

Thus in preparing scents from flowers the petals are heated in stills containing water, the steam carrying over the volatile oil into the condenser.

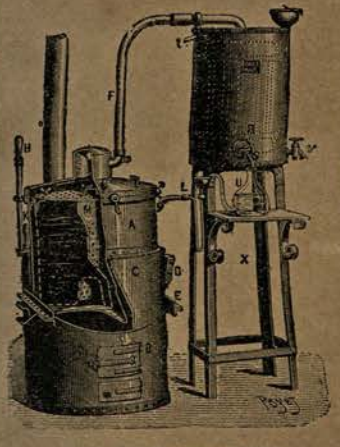


Fig. 48.—Perfume Still. (Manufactured by Egrot, Paris.)

Fig. 48 shows a still of this kind much used in France. It consists of a still A placed over a fire B. Inside A is a perforated copper basket M containing the flowers. The still is nearly filled with water, which, boiling, carries over the essential oil with the steam through F into the condenser R. The water and oil as it condenses discharges into the Florentine vase U, the essential oil usually collecting on the surface of the water, whence it is drawn off from time to time. The condensed water runs back through L into the boiler.

In the larger modern stills the steam is introduced from an outside boiler, and as the temperature and pressure can thus be better regulated there is less risk of overheating oils of delicate aroma.

In separating oils from lemon and orange peel and other products containing a large proportion of essential oil mechanical methods of expression are commonly employed, and distillation with steam is only used for separating an inferior grade of oil from the residues.

The rinds of such fruits as *limes*, *lemons*, *oranges*, *bergamots* are rich in essential oils—the so-called *citrus* oils—and much attention has been directed in recent years to expressing those oils

economically from them, an object all the more important as those rinds are, to a great extent, a waste product. The following are recent English Patents:—13,171, 1904; 6,036, 1909; 15,552, 1909.

An extraction method with a volatile solvent such as alcohol, or with olive oil or lard, is used in the preparation of delicate scents, the essential oils being subsequently separated from the extracts.

A typical modern extraction plant (Egrot's, of Paris) is shown in Fig. 50. The volatile solvent (alcohol, ether, benzene, carbon bisulphide) is raised by the pump into the collector D, which is provided with a glass gauge tube by means of which the volume of the contained liquid may be ascertained. The basket G, filled with plants, is lowered by means of tackle into the extractor A, which is then closed. Next the solvent from D is run into the heater E, containing a steam worm, and, according to its density, is thence sent into the extractor A either from above (by the pipe *b'*) or from below (pipe *b*), and comes out again by one of the pipes *c* or *c'*, after which, charged with perfume, it goes into the evaporator B by the pipes *d* and *f*. Here in B a heating coil vaporises the solvent, which passes as a vapour up the tube *g* into the condenser C and thence into the collector D, where it re-enters into circulation. The perfume remains behind in B. Finally the solvent is distilled off from the exhausted flowers in A. If alcohol is used as a solvent it soon becomes diluted with the moisture contained in the flowers. Consequently the alcohol is distilled away from A through a rectifier F, which only allows a sufficiently alcoholic distillate to pass. This is condensed in C and collected in D and used again; after which A is opened and the basket withdrawn and replaced by a basket filled with fresh flowers.

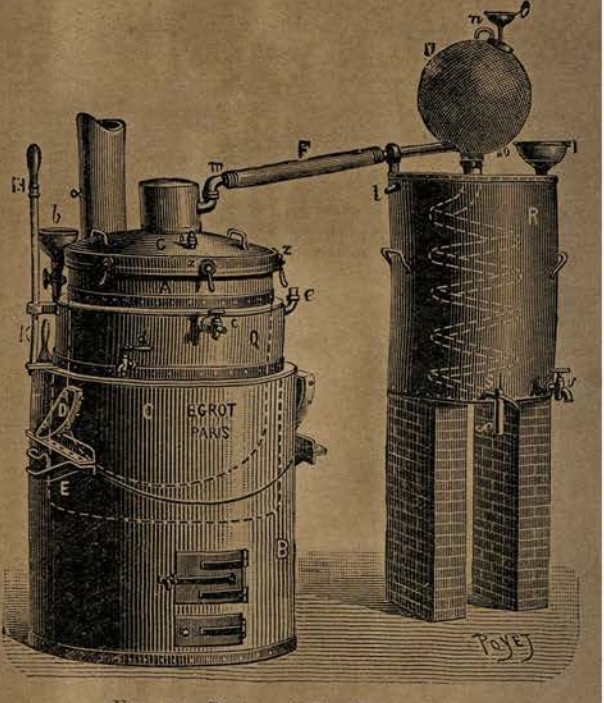


FIG. 49.—Perfume Still. (Egrot, Paris.)

Characteristics.—Essential oils differ widely from one another both in properties and composition, and it is not possible to classify them into distinct separate groups, as in the case of the fixed oils and fats.

Some are colourless, while others are green or dark brown in colour. In most cases they are lighter than water, but a few, like oil of cinnamon, are heavier. In some cases they readily undergo oxidation upon exposure to air and light; and hence it is usual for the manufacturers to send out orange or lemon oils in copper vessels the top of which is sealed with solder.

Frequently an essential oil is made up of several fluid constituents, while in other cases solid compounds (the so-called *stearoptenes*) are present in solution, and can be separated by chilling the oil. "Otto" of rose may be cited as an instance of this kind.

A high refractive index is a characteristic of essential oils, and its determination is one of the most important means of ascertaining the purity of an oil.

The compounds that have been isolated from essential oils include the hydrocarbon series known as terpenes, having the composition $C_{10}H_{16}$; alcohols and ketones related to the terpenes, such as borneol, $C_{10}H_{17}OH$, and camphor, $C_{10}H_{16}O$;

compounds typified by the alcohols, geraniol and citronellol; phenols and their derivatives; and aliphatic derivatives.

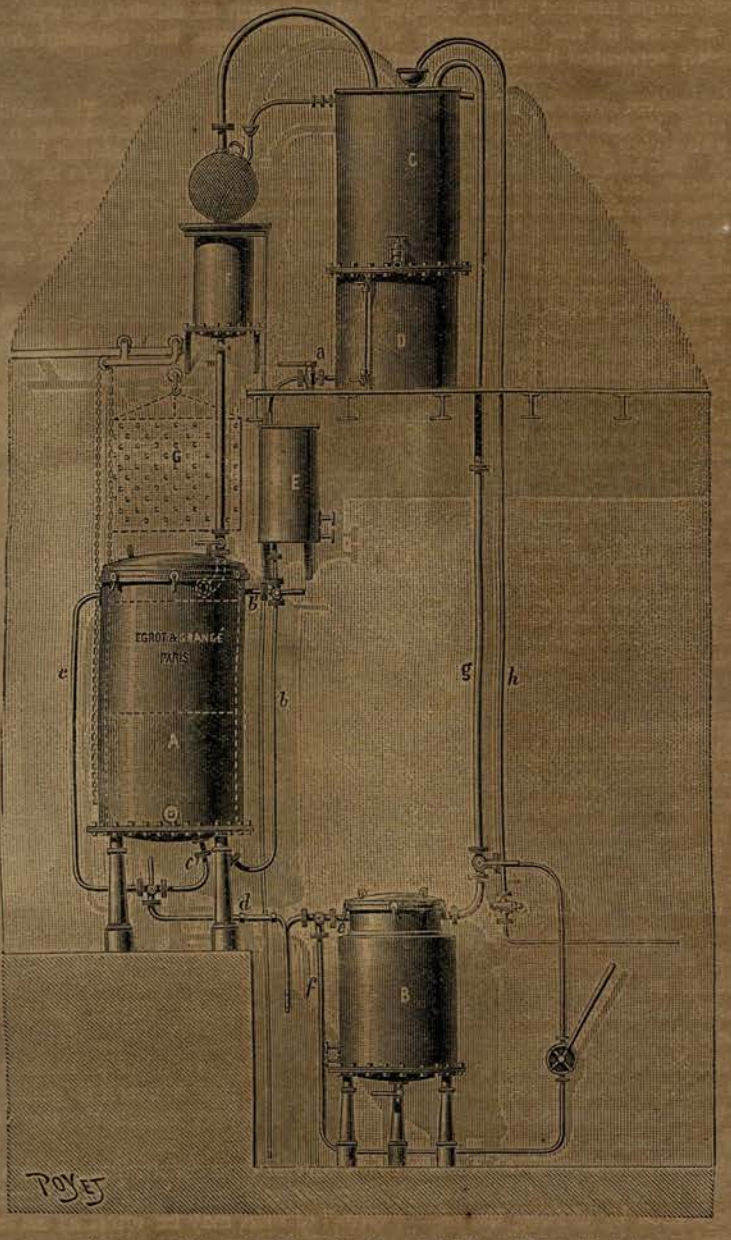


FIG. 50.—Extraction Plant for Essential Oils. (Egrot, Paris.)

Analysis of Essential Oils.—The estimation of the quantities and proportions of special compounds in an essential oil is of great importance in certain cases in which it pays to separate the active constituent and to sell it separately, and also

in the detection of adulteration when an oil containing a certain compound is mixed with another which does not contain it.

For instance, Japanese peppermint oil contains upwards of 80 per cent. of menthol, and a large proportion of this is frequently separated by a process of freezing, leaving only about 30-35 per cent. in the so-called "dementholised" oil, which is accordingly sold at a considerably lower price, and often used to adulterate untreated peppermint oils.

Again, clove oil should contain over 70 per cent. of the compound, eugenol, and should the proportion be much lower than this, the addition of an adulterant, such as oil of turpentine, is suggested; or a portion of the eugenol may have been removed and sold separately.

The essential oils which contain characteristic compounds, the estimation of which may afford data as to purity, include the following important products:—

Citronella oil (containing citronella); lemon-grass oil (containing citral); sassafras oil (containing safrol); bergamot oil (containing linalyl acetate); peppermint oil (containing menthol); (clove oil containing eugenol); lemon oil (containing citral); aniseed oil (containing anethol); oil of camphor (containing safrol); and eucalyptus oils (containing eucalyptol).

In addition to estimating the characteristic constituents of an oil, where this is applicable, the various physical properties are also determined, and the oil is separated by fractional distillation into several fractions which may then be further examined.

The specific gravity of essential oils may show great variations, as for example:—

Aniseed oil	0.9852	Clove oil	1.047
Bergamot oil	0.8808	Rose oil	0.8912
Lemon oil	0.8498	Turpentine oil	0.873

Thus an addition of, for instance, turpentine oil to clove oil would reduce the specific gravity below the normal figure.

The optical properties usually determined are the refractive index and the specific rotation. For instance, clove oil has a specific rotation of about $-4°$, while turpentine oil often has a rotation as high as $-75°$.

Again, lemon oil has a pronounced dextro-rotatory power (about $+60°$), whereas lemon-grass oil is nearly inactive in this respect ($+3°$ to $-3°$).

The solubility of an oil in certain solvents is in many cases a useful test. Thus citronella oil should dissolve completely in two to three times its volume of 80 per cent. alcohol at 20° C., whereas an oil containing paraffin oil, which is a common adulterant, is much less soluble.

The use of the distillation method is valuable, *e.g.*, in the examination of lemon oil, which is very frequently adulterated with oil of turpentine. Now since the latter has a considerably lower boiling point it can be concentrated in the first tenth of the distillate, and then detected by determining the optical activity of this fraction.

One of the most difficult adulterants to detect is an addition of terpenes, *i.e.*, the residual fraction left in the manufacture of so-called *terpeneless oils*. The latter are products made, for instance, from lemon oil by removing the inert substances (the terpenes) so that an oil with a much more concentrated flavour is obtained. Prepared oils of this kind are used in the mineral water industry, and give an improved flavour which more than compensates for the increased cost.

In cases where the residual terpenes have been used to adulterate, *e.g.*, lemon oil, the physical properties of the oil might be made so nearly normal as to make the oil seem genuine.

The adulteration of certain oils used in perfumery, such as rose oil, may also be done so skilfully that reliance must in the last resort be placed upon the judgment of a specialist who can discriminate between the odour of a genuine and an adulterated product.

Statistics.—The quantity of essential oil imported into the United Kingdom is shown below. Figures are also given showing the value of the *artificial* essential oils. (For these see next article by Dr Martin on **Synthetic Perfumes**).

	1908.	1910.	Value in 1910.
	Lbs.	Lbs.	
Natural essential oil	1,841,300	1,983,000	£320,000
Artificial essential oil	163,400	169,600	34,400

The United States in 1910 *imported* 415,000 lbs. of essential oils, of value $309,383. The *export* in the same year was 110,000 lbs. of *peppermint oil* (value, $216,000), and $322,000 value of other sorts.

XIII.—SYNTHETIC PERFUMES

By G. Martin, Ph.D., M.Sc.

LITERATURE

See under "Essential Oils."

Within recent years certain synthetic perfumes of great technical importance have been placed on the market. Perhaps the most important are **Ionone** (odour of violets) and **Vanillin** (aromatic principle of vanilla). Although most perfumes can be prepared synthetically from coal-tar products, yet in many cases they are merely separated in a pure state from less costly natural oils, sometimes by fractional distillation, and sometimes by other chemical actions. Thus, phenols, for example, are separated from aldehydes and ketones by their capacity for dissolving in caustic alkali; aldehydes and ketones (*e.g.*, citral) are separated by causing them to unite with sodium bisulphite; while sweet-smelling alcohols (*e.g.*, geraniol) may be separated by causing them to unite with anhydrous calcium chloride, or by esterifying them with dibasic acids and dissolving out the resulting esters with alkaline carbonates. The volatile products thus isolated are purified by distillation, the solid by crystallisation from organic solvents.

The scent industry has received a powerful impetus from synthetic scents, and Germany now turns out annually scents to the value of £2,000,000. The majority of the natural odours of flowers are due to complex mixtures of different scents. Almost all of these scents have been successfully reproduced by mixtures of synthetic scents, ranging from that of the violet to that of the rose. Although natural **oil of roses** contains about twenty different odorous substances, yet chemists employed by the German firms of Heine & Co., Schimmel & Co. (Leipzig) have succeeded in isolating all the components, synthesising these or preparing them from less costly oils, and then reuniting them in the proper proportions.

Synthetic attar of roses is now on the market.

Similarly **ionone**—an enormously powerful scent—is the basis of all violet-like scents.

In 1910 England imported 169,599 lbs. (=75.7 tons) of artificial essential oils, worth £34,370. Of this Germany contributed 140,000 lbs. (82 per cent.). The **natural** essential oils imported had a value of £320,000, and a weight of 900 tons.

The following are the chief synthetic (simple) perfumes, many of which occur naturally in essential oils:—

Alcohols

Citronellol, $C_{10}H_{20}O$.—Artificially made by reducing citronellal. Occurs in rose and geranium oil. Used for making artificial **Rose Oil.** B.P., 224-227.

Geraniol, $C_{10}H_{18}O$.—Isolated from palmrosa citron oil. Used as soap perfume, and for artificial rose oil. B.P., 230-232.

Linalol, $C_{10}H_{18}O$.—Isolated from linaloe oil, and used as a substitute for linaloe oil. B.P., 199-200.

Benzyl Alcohol, $C_6H_5.CH_2OH$, from benzaldehyde by reducing also by treating benzyl chloride with lead hydroxide and water. Used as a constituent of perfumes.

Phenylethyl Alcohol, $C_6H_5.CH_2CH_2OH$.—Prepared by reducing phenylacetic acid, $C_6H_5.CH_2.COOH$. Occurs in rose water and rose oil. Soluble in water. Used in producing a rose scent.

Cinnamic Alcohol, Styryl Alcohol, $C_6H_5.CH:CH.CH_2OH$.—Isolated from storax. Hyacinth odour. M.P., 33°; B.P., 255.

Menthol, $C_{10}H_{19}OH$.—Isolated from Japanese peppermint oil by freezing out; forms needles. M.P., 44°; B.P., 216. Used for peppermint oil, and in medicine.

Terpineol, $C_{10}H_{17}OH$, occurs naturally in different ethereal oils, and is produced artificially by reducing **Pinene**. Important constituent of many perfumes. Odour of hyacinths, hawthorn, or lilac.

Santalol, $C_{15}H_{25}.OH$.—Isolated by fractional distillation from sandal-wood oil. Used in medicine and perfumery.

Aldehydes

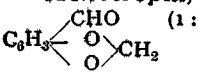
Citral, $C_9H_{15}.CHO$.—Isolated from lemon-grass oil. Used as a lemon aroma, and for manufacture of ionone. B.P., 227-229.

Citronellal, $C_9H_{17}.CHO$.—Isolated from the oil of the *Eucalyptus maculata*, var. *citriodora*. Used in perfumery.

Benzaldehyde, $C_6H_5.CHO$ (oil of bitter almonds, etc.).—Used as a soap scent. Manufactured on large scale. See p. 429.

Anis-aldehyde, $C_6H_4(OCH_3).CHO$ (1 : 4).—Prepared by oxidising anethol, $C_6H_4(OCH_3).C_3H_5$, or by methylating *p*-oxybenzaldehyde. B.P., 244° C. Hawthorn scent. Soap perfume.

Heliotropin, Piperonal.—Prepared from isosafrol by oxidation. Yellow crystals. M.P., 36-37. Heliotrope scent. Soap perfume.



Vanillin, $C_6H_3(CHO).(OCH_3)(OH)$ (1 : 3 : 4), occurs naturally in the vanilla pod and is prepared synthetically on the large scale by oxidising isoeugenol or eugenol, by introducing an aldehyde group into guaiacol, and by methylating proto-catechualdehyde. M.P., 82°. Used for perfuming food, and as a substitute for vanilla.

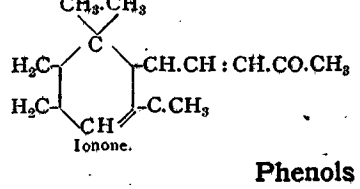
Phenylacetaldehyde, $C_6H_5.CH_2.CHO$.—Prepared by reducing phenylacetic acid, and from cinnamic acid. B.P., 210° C. Hyacinth odour. Soap perfume.

Cinnamic Aldehyde, $C_6H_5.CH=CH.CHO$, occurs in various oils; prepared by condensation of benzaldehyde with acetaldehyde. B.P., 125° at 15 mm. Substitute for cassia oil.

Ketones

Carvone, $C_{10}H_{14}O$.—Isolated from caraway, dill, and spearmint oils. Used for beverages, etc.

Ionone, $C_{13}H_{20}O$.—Synthetically prepared by condensing citral with acetone by means of alkalies and then treating with acids. B.P., 243-246° C. Most important "Violet" scent.



Ionone.

Phenols and Phenolic Esters

Carvacrol, $C_{10}H_{14}O$, and **Thymol**, $C_{10}H_{14}O$, are isolated parts of various essential oils.

Anethol, $C_6H_4(O.CH_3)(C_3H_5)$, occurs in oil of anise seed and other oils. Separated by freezing out. M.P., 21; B.P., 235. Important perfume.

Eugenol, $C_6H_3(OCH_3)(C_3H_5)(OH)$.—Isolated from oil of cloves by treating with KOH. Used for making **Vanillin**, also as a perfume for beverages. **Iso-eugenol** is isomeric with eugenol and is easily converted into it by alkalies.

Safrol, $C_{10}H_{10}O_2$.—Isolated on industrial scale from **sassafras oil** and used for making **Heliotropin**, also as a soap scent.

Nerolin, $C_{10}H_7.OCH_3$, β-naphthol-methyl-ether; smells somewhat like pine-apples. Soap perfume.

Oxides

Cineol, $C_{10}H_{18}O$, occurs in numerous ethereal oils. B.P., 177° C. Camphor-like odour. Cosmetic and soap perfume.

Fatty Acid Esters

See under Fruit Essences, p. 382. Important besides are—

Geranyl Acetate, Linalyl Acetate, Borneol Acetate, and **Amyl Salicylate.—Methyl ester of anthranilic acid** and homologues.

Lactones

Coumarin, $C_6H_4\begin{<}{O}{C_2H_2}\end{>}CO$, occurs in Tonquin beans, and is synthesised by Perkin's reaction from salicylic aldehyde and acetic anhydride. Important perfume.

Miscellaneous

Allylisothiocyanate, C_4H_5SN, is the active constituent of mustard oil, and is manufactured by distilling allyl iodide with alcoholic potassium thiocyanate, $CN.SK + C_3H_5I = CS.N.C_3H_5 + KI$. B.P., 151° C.

Artificial Musks are nitrated tertiary butyl alcohols made by various processes (see English Patents, 18,521, 1888; 4,963, 1889), but have no chemical relationship to real *musk*, whose odour is due to a ketone, $C_{15}H_{28}O$, of unknown constitution. Soap and toilet perfume.

Indol, C_8H_7N.—Prepared from indigo, and used for making synthetic **Jasmin oil**.

Nitro-benzene, $C_6H_5NO_2$, is sometimes used instead of benzaldehyde, the odour being somewhat similar. See pp. 422, 429.

SECTION II

The Sugar Industry

THE SUGAR INDUSTRY

I.—SUGAR

By G. Druce Lander, D.Sc., F.I.C.

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See under Starch for literature relating to Dextrin and Glucose.

Sugar to the chemist is the general name of a numerous group of organic compounds containing carbon, hydrogen, and oxygen, the last two in the proportion of 2 atoms of hydrogen to 1 atom of oxygen, the group being a division of the larger family of carbohydrates.

The chief classes of sugar are:—**The Monoses**, *hexoses*, $C_6H_{12}O_6$, represented by glucose, fructose, and galactose; *pentoses*, $C_5H_{10}O_5$, represented by arabinose and xylose. **Bioses**, $C_{12}H_{22}O_{11}$, represented by sucrose, maltose, and lactose. **Trioses**, $C_{18}H_{32}O_{16}$, raffinose, only those sugars of technological importance being mentioned. All the sugars are soluble, crystalline, neutral, and sweet compounds of vegetable origin, excepting lactose or milk sugar, which is the characteristic sugar of the milk of all mammalian animals. Numerous synonyms for the common sugars are in use, and may give rise to confusion. They are:—

Sucrose	cane sugar, saccharose, or sugar.
Glucose	dextrose, grape sugar.
Fructose	levulose, fruit sugar.
Lactose	milk sugar.
Maltose	malt sugar.

In technology "sugar" means **Sucrose**, $C_{12}H_{22}O_{11}$, whether derived from the sugar cane, beet, sugar palm, date, or maple.

In the following account of the technology of sugar no more can be attempted than to convey an idea of the chemical considerations, so far as they are known, which underlie the various steps; and to indicate the special chemical engineering problems which had to be solved in order to attain the modern high percentage of extraction from the natural juices. For details as to the numerous precautions and special points which have to be scrupulously observed in practice, reference may be made to the excellent special manuals of the subject.

SUCROSE (CANE SUGAR, BEET SUGAR), $C_{12}H_{22}O_{11}$

Properties.—Sucrose forms anhydrous, monoclinic crystals of sp. gr. 1.581 at 15° C. It is extremely soluble in water. A saturated solution at 15° C. contains 66.33 per cent. sugar.

A general formula for the solubility is per cent. sugar $= 64.1835 + 0.13477t + 0.0005307t^2$ (t = temperature ° C.).

The boiling points of sugar solutions at 760 mm. are:—

Per cent. sugar - -	10	20	30	40	50	60	70	80	90.8
Boiling point - -	100.4	100.6	101.0	101.5	102.0	103.0	106.5	112.0	130.0°C.

For the rapid analysis of the fairly pure sugar liquors in the works, specific gravity is taken by Brix or by Balling hydrometers, which indicate total solids, the Brix for cane, the Balling for beet juices.

For crude beet juice, on the other hand, this method will not work on account of the foreign extract matter. Hence the percentage of sugar in beet juice itself is always determined by the polarimeter.

Of special significance as regards the crystallisation of sugar from solution is the effect of mineral salts. These retard crystallisation, exercising a so-called "**melassigenic power**," which causes the sugar in molasses to be uncrystallisable. No satisfactory theory regarding this phenomenon has been put forward. It is usually held that 1 part of mineral salts (ash) will prevent the crystallisation of 5 parts of sugar. In commercial transactions raw beet sugar is **valued** on crystallisable sugar, *i.e.*, real per cent. sugar − ash × 5. (See p. 163.)

Sucrose is dextro-rotary, having at 20° $[\alpha]_D = 66.435 + 0.0087\ c - 0.000235\ c^2$ (Landolt)—c = concentration, *i.e.*, the number of grams per 100 c.c. of solution.

The rotation is slightly affected by foreign substances, particularly alkalis. Basic lead acetate first reduces and finally increases the rotation when added in increasing amounts, but the change is (with quantities used in practice) negligible in ordinary work.

When dry, sucrose melts without decomposition at 160° C., but enters into incipient decomposition even at 100° when moist, giving at the melting point glucose + fructosan ($C_6H_{10}O_5$); at higher temperatures by loss of water the dark coloured caramel is formed, whilst finally it carbonises, giving off carbon monoxide, formic acid, and other products.

On boiling sucrose solutions it is gradually hydrolysed or inverted—

$$\underset{\text{Sucrose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}$$

—more rapidly under pressure. This inversion is favoured by metals and hindered, by reason of alkalinity, by glass. Acids, as is well known, accelerate inversion in proportion to their dissociation constants, sugar being rapidly inverted in warm solutions by mineral acids, less readily by organic acids (acetic, tartaric, succinic, etc.)

Salts effect inversion if they suffer hydrolytic dissociation according to the nature of the metal and acid. Thus sulphates of zinc and copper being acid cause inversion, whereas salts of strong bases (alkali and alkaline earth metals) with weak acids (organic and carbonic acids) do not invert, and may by mass action check the inversion due to other salts.

Sucrose forms sucrates with alkalis, such as $C_{12}H_{21}O_{11}K$ which are alkaline and decomposed by carbonic acid. The sucrates of lime and strontia are of importance in technology. The mono- and disucrates of lime are soluble in water, decomposed by CO_2, and on boiling give insoluble tribasic sucrate, *e.g.*:—

$$3C_{12}H_{22}O_{11}CaO = C_{12}H_{22}O_{11}(CaO)_3 + 2C_{12}H_{22}O_{11},$$

which, when suspended in water, is also decomposed by CO_2.

Lime is consequently more soluble in sucrose solutions than in water, and similarly the prevention of the precipitation of copper, lead, and iron by alkalis in the presence of sucrose is referable to the

formation of sucrates. Calcium sucrate solution further also dissolves certain insoluble salts such as calcium phosphate, oxalate, etc., which are reprecipitated when the sucrate is decomposed by carbonic acid.

Sucrose forms unstable double compounds with salts, some of which may be got crystalline (those with alkali halides), others being viscous; this probably accounts for the melassigenic power above referred to.

Sucrose is acted on by many ferments. Thus by invertase of yeast it is transformed into invert sugar; it is also liable to the lactic butyric fermentation more characteristic of lactose. In cane juice it is liable to fermentation, giving rise to dextran, levulan, and ethyl acetate respectively.

SUGAR PRODUCTION OF THE WORLD, 1905-1909.*

COUNTRY.	1905-06.	1906-07.	1907-08.	1908-09.	1909-10.
CANE SUGAR.					
United States—	Tons.	Tons.	Tons.	Tons.	Tons.
Louisiana and Texas	348,752	243,000	352,000	370,000	335,000
Hawaii	383,225	392,871	465,288	477,817	490,000
Porto Rico	213,000	210,000	200,000	245,000	280,000
Total United States†	944,977	845,871	1,017,288	1,092,817	1,105,000
Cuba	1,178,749	1,427,673	961,958	1,513,582	1,700,000
Other West Indies	302,163	275,257	255,639	256,061	316,000
Mexico	107,529	119,496	123,285	125,000	130,000
Central America	18,516	19,747	19,258	21,000	21,000
South America	700,001	628,777	540,518	694,655	684,000
Total America	3,251,935	3,316,821	2,917,946	3,703,115	3,956,000
Asia	2,926,209	3,443,794	3,421,827	3,353,685	3,260,000
Africa	317,967	326,825	284,870	318,992	395,000
Oceania	230,000	249,000	280,725	231,098	217,328
Europe	15,722	16,400	11,000	20,000	16,000
Total cane-sugar production	6,741,833	7,352,840	6,916,368	7,626,890	7,844,328
BEET SUGAR.					
United States	279,393	431,796	413,954	380,254	457,562
Canada	11,419	11,367	7,943	6,964	8,802
Total America	290,812	443,163	421,897	387,218	466,364
Europe—					
Germany	2,418,156	2,239,179	2,129,597	2,080,000	2,040,000
Austria-Hungary	1,509,789	1,343,940	1,424,657	1,398,000	1,260,000
France	1,089,684	756,094	727,712	802,000	825,000
Russia	968,500	1,440,130	1,410,000	1,265,000	1,150,000
Belgium	328,770	282,804	232,352	258,000	250,000
Netherlands	207,189	181,417	175,184	214,000	200,000
Other countries	410,255	467,244	462,772	500,000	460,000
Total Europe	6,932,343	6,710,808	6,562,274	6,517,000	6,185,000
Total beet-sugar production	7,223,155	7,153,971	6,984,171	6,904,218	6,651,364
Total cane and beet sugar	13,964,988	14,506,811	13,900,539	14,531,108	14,495,692

* In long tons of 2,240 lbs., except in the case of European beet-sugar production, which has been retained in metric tons of 2,204.622 lbs., as estimated by Licht. United States beet-sugar data were obtained from reports on the Progress of the Beet-Sugar Industry in the United States; other data from official statistics of various countries, and from Willett and Gray.

† Not including the Philippine Islands, which are included under Asia.

Pure sucrose is not oxidised by Fehling's solution, the gradual reaction being attributable to inversion.

Production of Sugar.—The only sources of great commercial significance are from the juices of the cane and sugar beet. The sugar palm, date, sorghum, and maple are worked for sugar, which, however, chiefly finds local use. As regards distribution, cane is a tropical plant or sub-tropical indigenous to Southern Asia, and beet is a temperate zone crop. The annexed table from the U.S. Report on "Progress of Beet-Sugar Industry in 1909," indicates both the geographical distribution and output in tons of sugar.

The British importation for 1908, 1909, and 1910, in tons, was:—

	1908.	1909.	1910.
European refined (beet)	940,987	944,372	846,862
Raw beet	493,721	522,175	319,703
Raw cane	240,420	292,959	562,165
Total	1,675,128	1,759,506	1,728,730
Per cent. beet	85.7	83.4	67.5
Per cent. cane	14.3	16.6	32.5

The average value per cwt. was 15s. 10d. for refined, and 12s. 10d. for unrefined.

Sugar cane contains on an average:*—Sucrose, 11-16 per cent.; reducing sugar, 0.4-1.5 per cent.; ash, 0.5-1.0 per cent. Other constituents are fibre (10-15 per cent.), pectin, nitrogenous matter (0.6 per cent.), and organic acids.

Beet juice contains about 15 per cent. sucrose and 5 per cent. non-sugar (ash 0.8, nitrogenous 1.6, pectin, dextrine, raffinose, and minor constituents).

The per cent. sucrose of the total solid matter is the "quotient of purity" and is a guide to the quantity of crystallisable sugar.

The sugar content of the **beet** has been improved since 1840 from about 6 per cent. by careful selection, only those roots showing a high sucrose per cent. being used for seeding. Occasionally beets contain over 20 per cent. sucrose. In the season 1908-09 the German average was 17.63 per cent., and for that season beets containing as much as 28 per cent. were noted. The average sugar yield per acre in Germany is 1.83 tons, the highest in Europe, the general European average being 1.47 (Russia, 0.81, Germany, 1.83).† As a rule high sucrose per cent. is found along with a low tonnage of crop.

The yield of sugar from **cane** varies, averaging about 4 tons, and sometimes reaching over 5 per acre.

The cost of production depends mainly on sugar content, and may be stated approximately at 9s. per cwt. under the most favourable conditions. In the good 1908-09 season it fell to 8s. 6d. in Germany. The cost of cane is less by about 1s., and so low a figure as 6s. 6d. is quoted by Martineau.

It has been repeatedly shown that good beet crops can be raised in Great Britain. Among recent demonstrations may be mentioned the Suffolk tests of 1906, reported on by the East Suffolk Chamber of Agriculture. The average crop of twenty independent trials was 14 tons 17 cwt. per acre of roots, containing 16.21 per cent. sucrose, of purity coefficient 87.3. The lowest yield was 6 tons 6 cwt., giving 15.96 per cent. sucrose, of purity 89.7 (suffered from drought); the largest yield was 25 tons 10 cwt., giving 14.8 per cent. sucrose, of purity 83.0; the highest sucrose per cent. observed was 19.4, of purity 90.8, in a yield of 14 tons.

A sample grown in Essex (1910) was found by the writer to give sucrose 15.6 per cent., with a purity coefficient of 92.8.

* From Prinsen Geerligs' "Cane Sugar."
† From G. Martineau, "Sugar."

The stages in the technical extraction of sugar may be divided into (1) Preliminary treatment; (2) Preparation of dilute extract by expression or solution; (3) Purification or removal of extraneous organic matter (gums and proteins); (4) Concentration to thick syrup; (5) Boiling to crystallisation or strike point; (6) Crystallisation; (7) Turbining, or centrifugal separation from molasses.

The later stages of this series (4-7) are alike for beet and cane, the other operations differing chiefly in detail. The operations will be outlined for the **beet extraction** first.

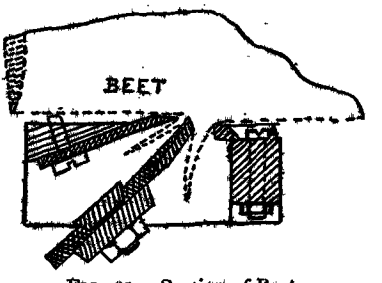


FIG. 51.—Section of Beet Slicing Knife.

1. The **preliminary treatment** consists in topping, which is done on the field, thoroughly cleansing, drying, weighing, and slicing the roots. Washing to remove earth and stones is performed by running the roots in a stream of water, in which a rotating axis having specially arranged wooden arms agitates them and drives them forward, stones sinking, and lighter impurities being removed by the reverse water current.

More compact machinery is sometimes used, for example in Raude's system, in which the roots are fed into a vertical cylinder of water in which helices are working. They sink, are driven to the periphery, and then upwards by the screws to the exit, from which they are taken on an endless screw. The cleansing in such cases is caused by the rubbing of the roots together, and requires that the machine shall be kept full.

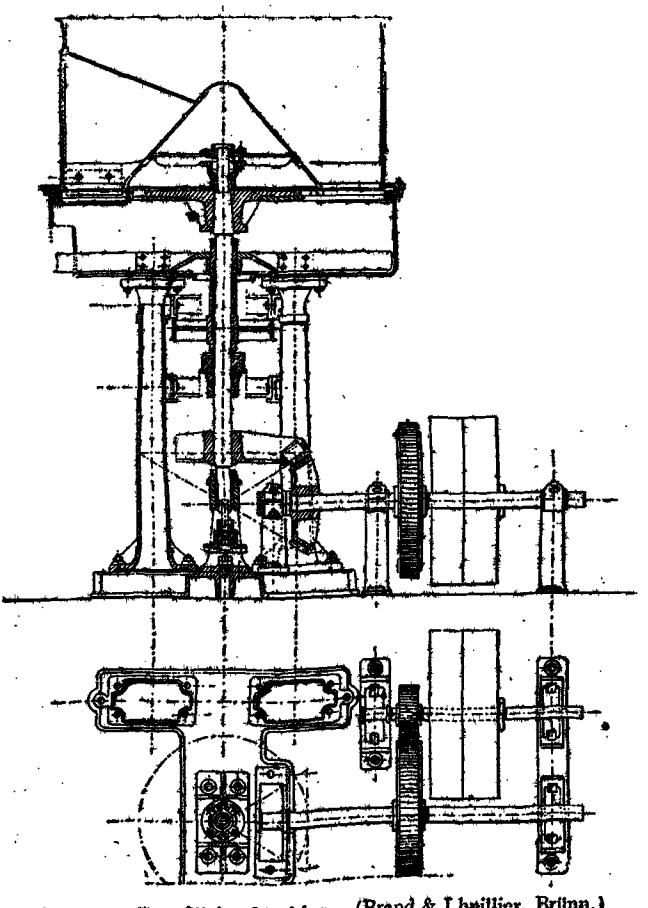


FIG. 51a.—Beet Slicing Machine. (Brand & Lhuillier, Brünn.)

The beets are then sliced. They are fed into a hopper from which they pass on to a horizontal circular disc carrying knives by which they are cut into slices.

The most usual form is V-shaped, like the ridge tile of a roof, a form which tends to prevent close packing, a desirable point in the subsequent diffusion. The discs vary from 1.2-2.5 metres in diameter. The knives are fixed into holders, which can be easily taken off or fixed, and it is of great importance that they should be very keen, so as to give well-cut slices.

2. **The Preparation of a Solution—Diffusion.**—Expression of the juice has been abandoned now for many years in the beet industry. The diffusion process (Robert, 1860) takes advantage of the phenomenon of osmosis through the cell wall. When immersed in water,

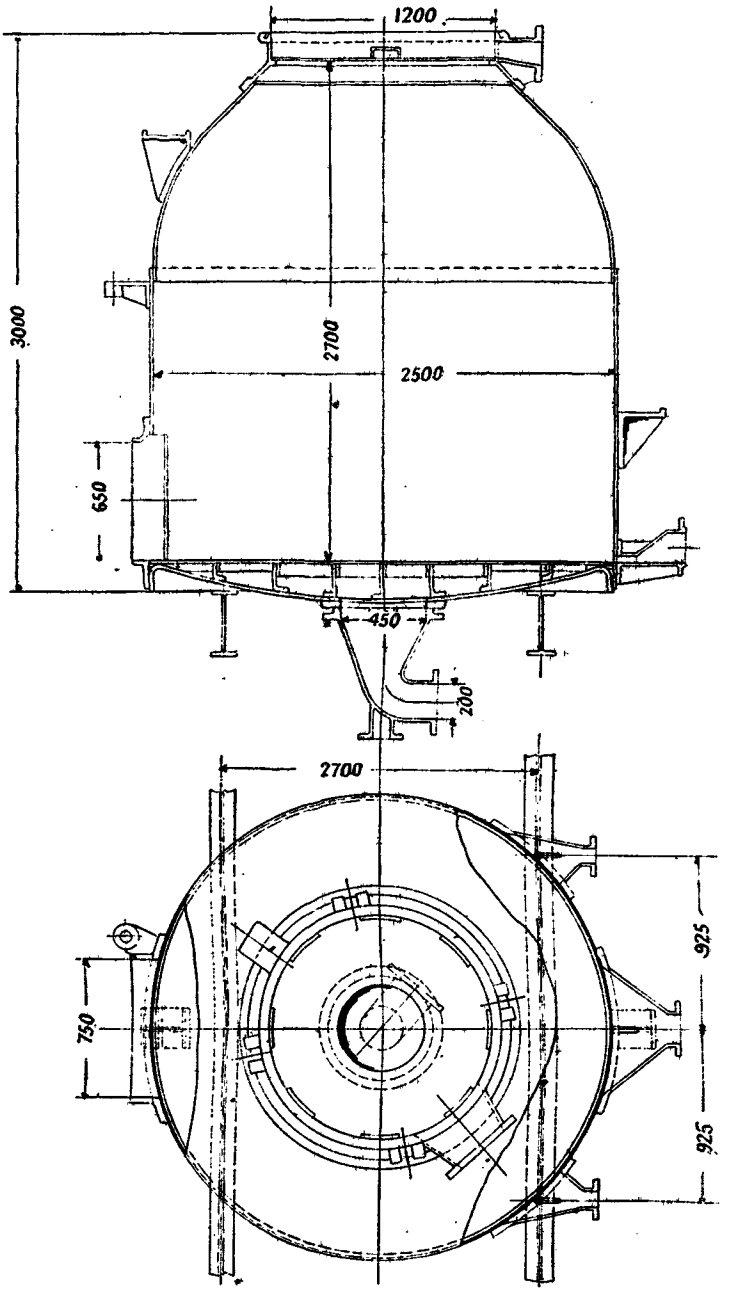


FIG. 52.—Diffuser of 115 Hectolitres Capacity. (Brand & Lhuillier, Brünn.)

sucrose, salts, and the simpler organic acids and amino-acids are permeable, whilst pectins and proteins are retained in the cell. Such small quantities of these latter as are found in the diffusates are derived from cells which have been cut or torn in slicing. The thin syrup of diffusion is therefore purer than the plant juice.

Further, diffusion may be made exhaustive and economical by allowing the water from partially exhausted slices to pass on successively to fresh ones, thus ensuring the continuity of the operation and the production of diffusion juice in the ratio of not more than 115 to 100 of cell sap, which shall contain practically all the sugar. Or manifestly, if desired, any percentage of sugar may be left in the slices as is done in the Steffen process, where about 3 per cent. of sugar is not extracted.

A diffusion battery consists of several cells or diffusers arranged either in rows or in a circle, the number of cells varying from eight, but in modern work usually being from fourteen to sixteen. The diffusers are cylindrical iron vessels of from 4,000 to 8,000 litres capacity, and having on the average

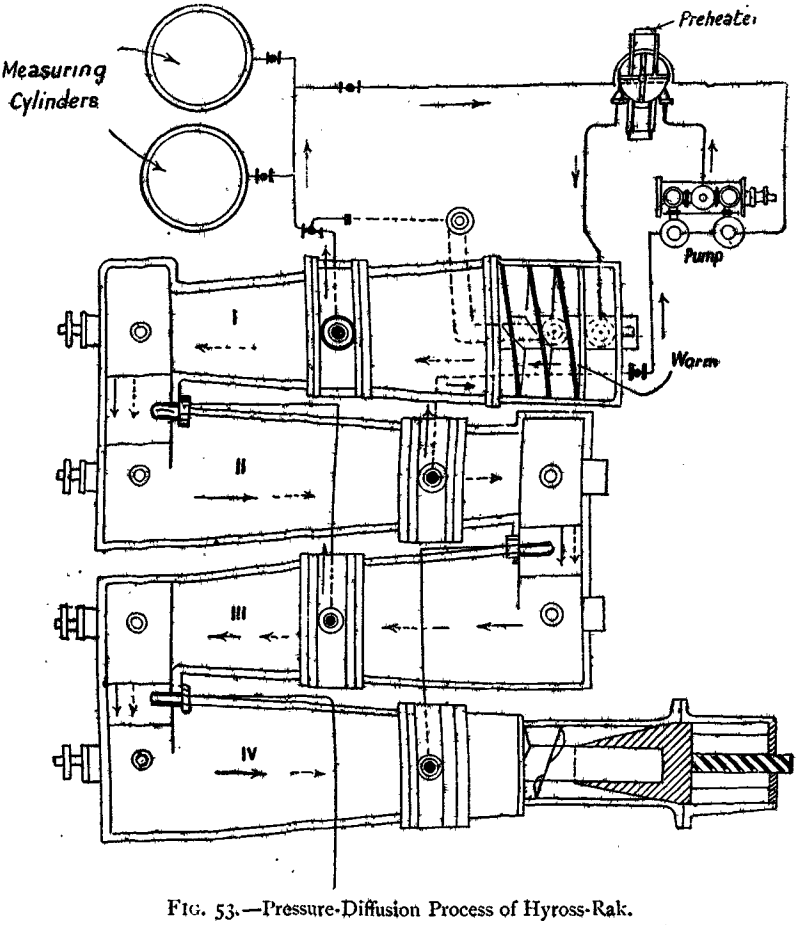


FIG. 53.—Pressure-Diffusion Process of Hyross-Rak.

the ratio 1 : 1.3 of diameter to height, provided with manholes at the top for feeding, and having discharging doors either in the base or at the side. Calorisators may be interposed between the cells, or heating may be effected by steam injection.

The temperature for diffusion is from 70°-80° C. which should not be exceeded. The higher temperatures are better for sound beets and rapid work.

The lowest theoretical volume of diffusion juice is 94-95 per cent., that is, the sap content of the roots. In practice 105-106 per cent calculated on the roots is usual. Higher dilution may mean more thorough extraction, but this may be commercially nullified by the greater fuel consumption required for evaporation. From 0.15-0.35 per cent. approximately of residual sugar in the slices represents the limit of extraction.

In the working of a battery, that diffuser which has been freshly filled is charged with warm, nearly concentrated, juice, which can take up a little more sugar, and then with juices of diminishing

strength down finally to fresh water, which passes on through successive diffusers to saturation. The last charge of water is usually admitted from below in order to loosen the mass of slices so as to facilitate the discharge of the exhausted slices, which are expelled by compressed air or water. The first cell of the series (*i.e.*, the one freshly filled) is charged under pressure, which serves to propel the juice from cell to cell of the battery. The time occupied for a battery of sixteen diffusers will be about six minutes for each cell, or ninety minutes for the battery.

In modern work certain variations in practical respects are in vogue. Hot diffusion systems (Malichar-Cerny, Naudet, and Köhler) have for their object the formation of more concentrated juices by working rapidly at 85°, and further, by reason of albumen coagulation, the production of purer thin syrup. Saving in fuel and lime is thus effected.

In Kaiser's process the fresh slices are warmed by spent steam to about 70° before washing with juice.

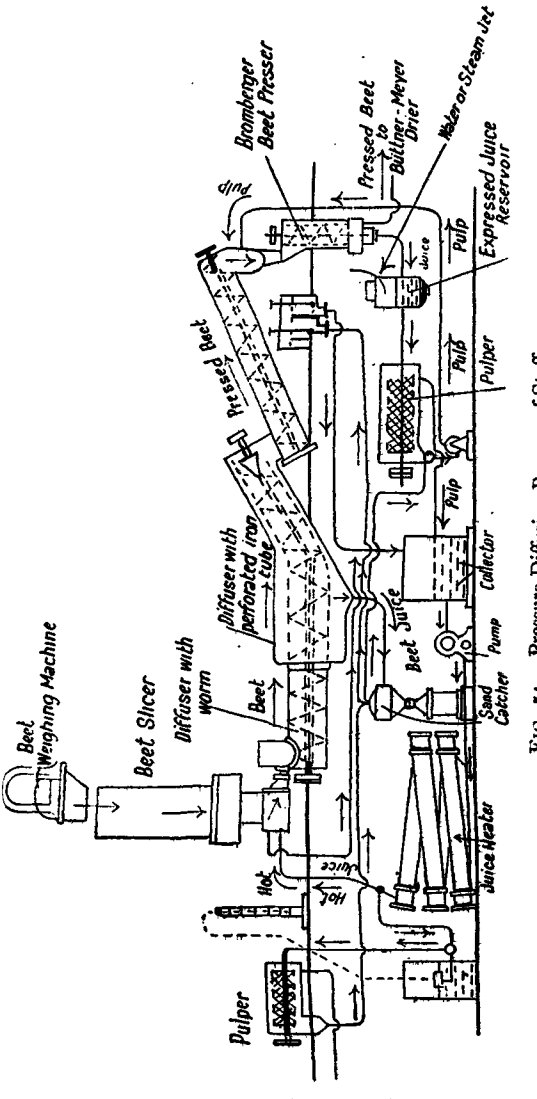


FIG. 54.—Pressure-Diffusion Process of Steffen.

The **pressure-diffusion processes of** Hyross-Rak and Steffen aim at the utilisation of the diffusion waste water, and the preparation of a more or less sugary diffusion slice for use as a cattle food. Since, as the result of the operation of the Brussels Convention, cane sugar has been able to compete on even terms with Continental beet sugar, and in consequence supply having overtaken demand, the value of 88° sugar is little in excess of the cost of production, attention has been turned increasingly to the support of the sugar industry by the preparation of high grade dry slices for feeding stock.

Obviously such extraction methods must be combined with the installation of slice-drying plant.

In **Hyross-Rak's process** (Fig. 53) the slices are forced by an Archimedean screw through several diffusers arranged laterally. In the first, fresh slices are in contact with more concentrated juice and from this unit the thin syrup is withdrawn. In following units the successively poorer slices are in contact with thinner juices. The cells are cylindrical at the beginning, conical thereafter, and open into enlarged spaces from which an ingenious propeller transfers the slices to the wide end of the next cell. In spite of the 180° turn of the moving mass it is claimed that the process is quite continuous. The water consumption is given as 25-30 litres per 100 kilos of slices, the residue having 22 per cent. dry matter of 2.6-3.9 per cent. sugar content. Roots of 16.5-16.7 per cent. sugar gave juice of sp. gr. 1.0742, having 88.5-89.5 purity.

In **Steffen's process** the roots pass from a weighing machine to a slicer, where slices of 1.5 mm. thickness are cut (Fig. 54). From the slicer they are carried through an inclined tube by hot syrup at 92°-97° into the diffuser consisting of a horizontal tube, in which the slices are at 82°-85°, leading to a second tube of perforated iron where separation of juice from slices takes place. The third element s an inclined tube, also perforated and built with the second into the same juice chamber. In it

the slices are lifted from the syrup and at the upper end submitted to preliminary pressure. Thence the slicers pass to a final inclined tube where mashing takes place and pass on to slice presses. The slices remain three minutes in the brew vessels and the whole interval up to completed pressing is about ten minutes.

Diffusion slices, or pulp, result in the proportion of about 85 per cent. of the original roots. Undried slices contain on the average 6 per cent. of total solids and 94 per cent. water. About 0.2 per cent. of sugar remains in the pulp, excepting in the Steffen or similar processes, when about 3 per cent. remains.

By pressing, the total solids may be raised from 6 to 10 or 15 per cent., *i.e.*, the yield of pulp may be reduced from 85 to 51 or 34 per cent. respectively. But strong pressure involves some loss of nutrient substance and pulp, and will therefore only be employed when it is intended to dry the pulp, in which case the saving of fuel will compensate the loss in question.

Pulp presses for the most part consist of Archimedean screws on perforated axes working within conical perforated cylinders. As the pulp is driven forward it is compressed, the water draining away by the perforations in the axis and wall of the cone. An installation may be made in which the pulp elevators end in conical press cylinders.

It is to be remarked that those processes in which the diffusion press water is returned to the batteries as above mentioned effect saving both of sugar and other nutrient substances, as well as solving the problem of waste water disposal.

Wet slices are often fed direct to farm stock, or are "siloed," that is, stacked in large heaps, when fermentation sets in with production of acidity due chiefly to lactic acid, and a fall in protein occurs. Wet slices do not, however, possess very great durability or commercial value, and in very many modern Continental works drying plant has been installed. Two systems are operated, namely, fire drying by furnace gases according to Büttner-Meyer, and steam drying according to Sperber, the former being more usual.

The composition of dried slices varies; the subjoined figures from Stift-Gredinger, "Zuckerrübenbau," illustrate this point.

	Ordinary Slices.		Steffen Sugar Slices.*	Hyross-Rak (Steam-Dried).†
	Fire-Dried.	Steam-Dried.		
Water	4.19-15.80	8.36-11.76	6.05-13.0	2.79
Protein	4.50-8.81	6.69-10.25	5.80-7.0	7.56
Amides	0.06-1.31	0.12-0.25		0.88
Fat	0.22-1.80	0.51-1.15	0.30-0.50	0.23
Carbohydrate	47.70-62.73	55.14-60.64	66.50-69.10	61.45
Fibre	13.60-22.84	18.45-21.60	10.50-19.95	21.76
Pure ash	2.63-5.96	3.18-4.97	3.50-5.0	2.82
Sand	0.02-2.94	0.04-1.13		2.51

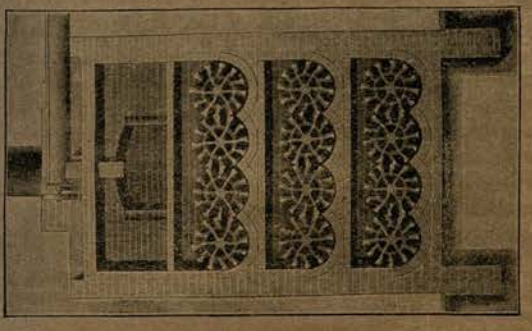
In the **Büttner-Meyer system** (Fig. 55) the wet slices are fed into an oven, built into which are three tiers of horizontal rotating shafts having blades by means of which the slices are turned and propelled forward from set to set of agitators. In the opposite direction to that of the slices passes a current of mixed furnace gases and air, entering the kiln at 800°-1,000° C. By this hot current the slices are rapidly dried, and by reason of evaporation do not probably go above 100° C. Drying is not, however, pressed too far in case of fire.

In **steam-drying according to the Sperber method**, the slices after wet pressing are ground—to facilitate drying—and fed into an iron chamber having four double-walled iron troughs, heated by spent steam. Each trough is provided with a pipe calorisator heated by live steam at 4-5 atmospheres, and with transport blades. The divided mass is thus passed along the first trough, on to the second, third, and fourth, alternating in direction. The disengaged steam is withdrawn by an exhaust, which also draws in warm air, a partial vacuum being produced, which aids drying.

* Containing 30.0-38.4 per cent. sugar.

† Containing 12.6 per cent. sugar.

3. **Purification of the Thin Syrup.**—Diffusion juice averages 11-15 per cent. sugar, and 13°-17° Balling, showing purity of 85.5-89.66, invert sugar not exceeding about 1 per cent., and ash being about 2.5-3.5 per cent.



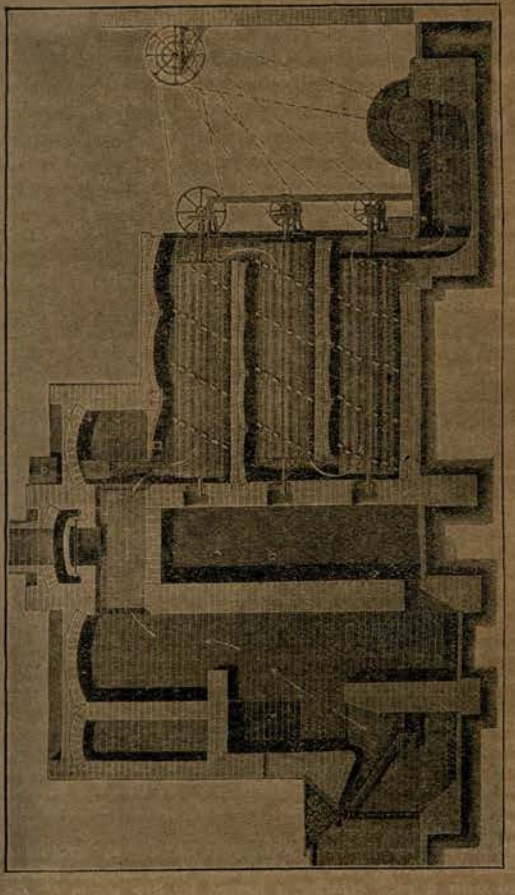


FIG. 55.—Büttner & Meyer's Slice Drier.

Vegetable detritus from the batteries must be removed, and this is done by pulp filters, which are cylindrical fine sieves, in a wider containing cylinder. The juice, in passing through the filter, leaves solid particles on the sieve, which must be cleaned from time to time.

All practical systems of purification depend on the use of lime, which has been practised for many years. In simple "defecation," after admixture with milk of lime and heating, the scum is removed. The great difficulty is in mixing the correct quantities. An excess of lime is prejudicial, since it acts on the reducing sugars: moreover, loss may occur through formation of the insoluble tribasic calcium sucrate. These irregularities are entirely overcome by "carbonation," which is universally employed in the beet industry. The general principle of carbonation is the treatment of the warm juice with milk of lime and precipitation of carbonate therefrom with carbon dioxide. Any insoluble sucrate is thus decomposed, and the voluminous precipitated chalk carries down with it proteins and pectins, probably by absorption. This effect is similar to that of lime in the clarification of sewages, and the removal of colloid impurities is possibly a physical and not a chemical reaction. Most of the organic acids, notably oxalic, are also precipitated as lime salts.

Carbonation brings about a remarkable improvement in the mobility and colour of the juice, which becomes quite clear and limpid.

Before treatment with lime the juice is warmed. On leaving the diffusers it has a temperature of

20°-35° C., and before liming it is raised to about 80°-85° C. with the object of coagulating some of the protein, which is thus rendered less liable to decomposition by the alkali. Sometimes the albumen is filtered through cloth, but this does not seem to be of special advantage.

Liming is performed either by means of milk of lime or by the immersion of lumps of quicklime.

In the "wet process" by milk of lime the warm juice is run into cylinders or "malaxeurs," holding from two to three times the volume of juice from one diffuser, having an iron stirrer making ten to fifteen revolutions a minute. From above the calculated quantity, either measured or weighed, of cream of lime is added.

Special measuring vessels are used in which the weight of CaO delivered is shown on a graduated scale by pointers worked by floats in the cream of lime. On the average the addition of lime is in the proportion for 100 of roots for the first saturation of 2.5-3 per cent. CaO, and for the second saturation 0.25-0.5 per cent. CaO.

The quantity of milk of lime to be added and the volume change of juice resulting are to be exactly calculated. For instance, supposing it is desired to add 3 per cent. of lime to a juice of 115 per cent., and that the milk of lime has 20° Beaumé, a gravity corresponding to 206 g. CaO per litre; we have 3 kilos lime (to the 100 kilos roots) in 3,000 : 206 = 14.56 litres milk of lime, weighing 14.56 × 1.162 = 16.92 kilos. Or about 17 per cent. calculated on roots, or 12.66 per cent. by volume, calculated on dilution 115 per cent. Further, the dilution is 16.92 − 3 = 13.92 per cent. of water on roots or 12.1 per cent. on diffusion juice.

"Dry liming" must be effected by immersing the quicklime in a flat sieve in the juice which is kept actively circulating by stirrers. Otherwise considerable local superheating due to slaking will occur, with corresponding decomposition of the sugar solution.

Opinion varies as to the relative advantages of wet and dry liming. The solubility of quicklime in sugar is greater than that of slaked lime on account of the readier formation of sucrates by the former agent, and it is claimed that clearer syrups are got therefrom. In dry liming dilution is avoided, but on the other hand in wet liming the liquor from the lime filter presses can be used for slaking, whereas in dry liming it has to be evaporated, so that this advantage is cancelled. For dry liming 85° of heating is desirable else the decomposition of amides is incomplete. In the event of invert sugar being present dry liming tends to its decomposition, the products forming coloured iron salts. In neither process does the lime sludge from the filter presses contain notable quantities of sugar.

The juice having been limed passes to the "saturators," tall four-sided or cylindrical iron vessels, into which the carbon dioxide is pumped and injected into the liquid under pressure through various types of gas dividers (Fig. 56).

Only about one-third to one-half of the gas is absorbed, the remainder passing out of the saturator. Temperature is maintained by a copper steam coil. At first the juice foams greatly, and has a somewhat gelatinous consistency, being unfilterable. Foam is destroyed by the sparing introduction of oil (tallow or castor oil) or by blowing steam direct on to the surface. As saturation proceeds the current of gas is increased, and the precipitate shows greater tendency to settle.

When an alkalinity of 0.05-0.06 per cent. by phenolphthalein titration, and reckoned as CaO, is attained the first saturation is finished in from twelve to fifteen minutes.

Continuous carbonation is designed to secure more complete absorption of the gas. The current of gas is divided by means of a turbine, and distributed through the mass of juice in a saturator of the ordinary type, having at a height of about 2 metres an outlet conducting the liquid to a second similar tank. The gas and juice outlet valves being opened, the admission of juice is so regulated that it passes over into the second saturator with an alkalinity of about 0.14 per cent., and is then saturated further, so that a continuous stream of 0.05-0.06 per cent. CaO may leave the installation.

After passing through a sand and stone trap the turbid fluid is pumped to the filter presses. These are all based on the well-known Dehne frame-press system, p. 34.

Washing of the sludge cakes is necessary, the degree of washing being determined by considerations of fuel consumption involved in extra evaporation, and is seldom pushed to the limit. Unwashed sludge cake forms about 12 per cent. reckoned on the weight of roots, and contains about 60 per cent. of syrup, equivalent to 7-8 per cent. of sugar, thus meaning a loss if unwashed of about 1 per cent. of sugar reckoned on the roots.

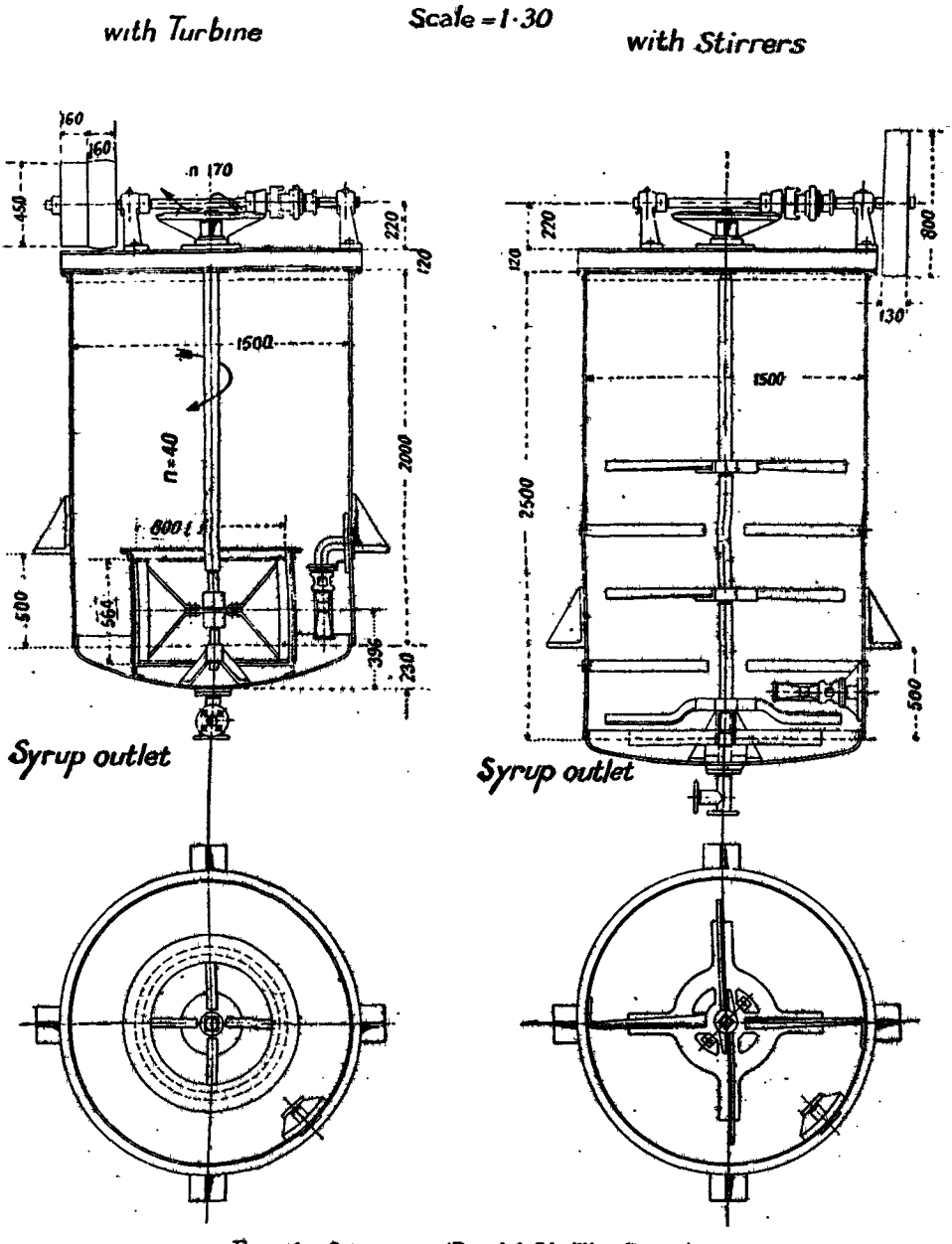


FIG. 56.—Saturators. (Brand & Lhuillier, Brünn.)

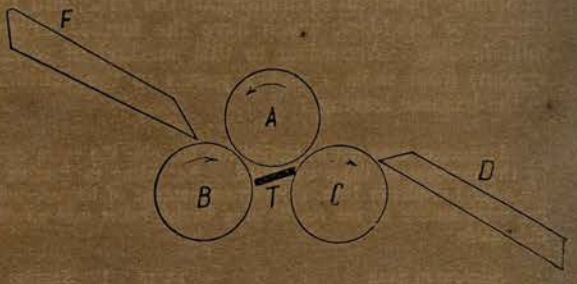
The sludge cakes, which have manurial value, vary in composition according to figures quoted by Stift-Gredinger as shown :—

Water	30.08 to 59.31	Nitrogen	0.12 to 0.41
Chalk	28.6 ,, 50.00	Phosphoric acid	0.50 ,, 2.22
Lime	0.10 ,, 1.51	Organic matter	7.11 ,, 12.1
Potash	0.04 ,, 0.40		

Second saturation follows the same course as the first, the preliminary heating

being to about 90° C., and the liming being to the extent of 0.1-0.5 per cent. A third saturation is sometimes adopted, which may be done by carbon dioxide, or by sulphur dioxide, or a mixture of both. Sulphitation of the thin syrup effects decolourisation, and the traces of sulphite remaining in the juice act as a preservative, but are liable to form incrustations in the subsequent evaporation, so that generally sulphitation is applied to the thick syrup.

Lime burning is manifestly an integral part of sugar factory routine, yielding both the lime and carbon dioxide required. Details of this process are in this connection superfluous.



SECTION OF CANE SUGAR CRUSHING ROLLS

FIG. 57.

The **preliminary treatment of cane** for the extraction of juice and its clarification necessarily differs from that followed with beet partly on account of the different form and texture of the plant, and also from the fact that in most cane districts fuel is scarce, and the residual fibre, or "bagasse," forms the needful combustible.

The canes are fed as regularly as possible into crushing mills.

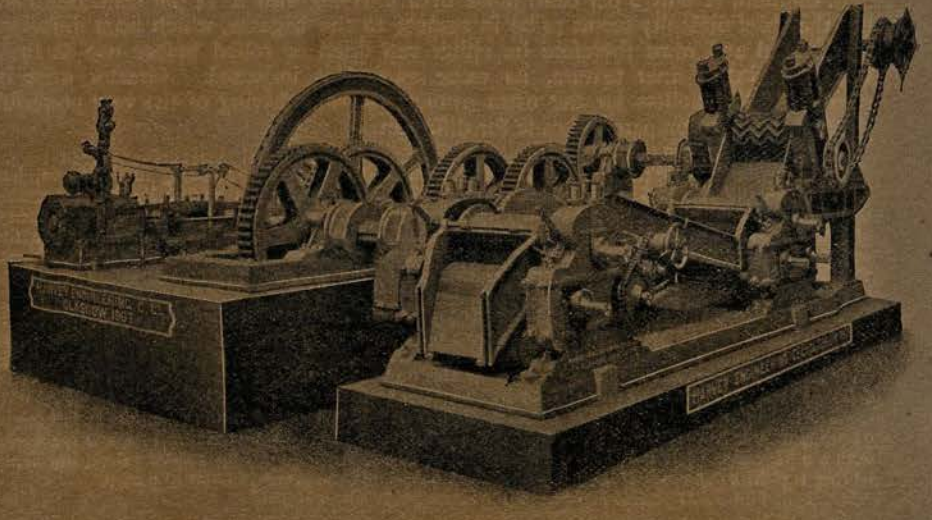


FIG. 58.—Double Crushing Plant with Krajewski Crusher in Front.
(Harvey Engineering Co., Glasgow.)

These usually consist of three smooth rollers, two on one level and the third above, rotating as shown by the arrows (Fig. 57).

The canes are fed along F to the combination AB, or the feed roller, where they are crushed, and directed by the adjustable curved plate or "trash" T to the bagasse roller AC, where expression of juice chiefly takes place. The bagasse passes along D. Combinations of thee-system rollers are in general use, often combined with a preliminary crusher of the Krajewski type, consisting of two rollers having V-shaped teeth whereby the work of the first mill is relieved.

It is obvious that no crushing can effect a complete expression of juice, and maceration of the crushed bagasse is resorted to. Upon leaving the rollers the compressed fibrous mass on expanding is able to take up water fairly thoroughly, although not so completely as to fill up all the cells. Maceration with the last mill juice of the bagasse leaving the first mill may be performed if the crushing is sufficiently powerful to disintegrate the cane, and this may be secured by means of cutters or shedders, which have the further advantage of securing more regular mill feeding. According to this method of working, the juice (in a three-mill system) from mills 1 and 2 passes to the clarifiers, that from 3 being returned to the bagasse leaving 1.

Maceration must not be carried too far, else the extra cost of evaporation will not be covered by the increase of sugar extracted. According to Prinsen Geerligs 12-16 per cent. maceration gives good results in Java, the sucrose content of bagasse being 4.5 per cent. Figures quoted by the same author of the results of a twelve-roller mill afford a good idea of the kind of results obtainable.

Sucrose in cane	15.37	Sucrose lost in bagasse on 100 cane	0.76
Fibre in cane	10.98	Extraction on 100 sucrose in cane	95.40
Sucrose in bagasse	3.28	Dilution by maceration on 100 normal juice	26.12
Moisture in bagasse	45.66		
Fibre in bagasse	49.92		

In consideration of the loss of sucrose, and further of the expression of objectionable colloidal impurities, very naturally much attention has been directed to the practicability of diffusion for cane extraction, but diffusion is not applicable in practice for several reasons. Although the juice contains less impurity, diffusion in test experiments quoted by Geerligs gave a 95 per cent. extraction, with a 25 per cent. dilution, or only 2 per cent. more than crushing with a 14 per cent. dilution. But the chief difficulty seems to be in respect to the bagasse, which from diffusion is saturated and must therefore be either sun dried or rolled before use as fuel, whilst, having a finer texture, its value as fuel is impaired. Greater work is thrown on the boilers for the extra evaporation and driving of the very powerful slicers needed to prepare the cane for diffusion.

Crushing with subsequent systematic lixiviation of the bagasse, according to Perrichon, has been successfully practised in Egypt. The bagasse is fed into waggons having sieve false bottoms and discharge valves, and holding about 1¾ tons of bagasse. Hot water is run on to the contents of the waggon, and after about seven minutes drawn off, and pumped up to a tank above the waggon levels, whence after reheating it passes to a second waggon, and so on over nine waggons. This system gives probably about 15 per cent. dilution, and accomplishes an extraction equivalent to 96.7 per cent. on juice.

In the Naudet process the bagasse from a double mill is charged into a diffuser in which it is mixed with cold mill juice. The juice is drawn off by a centrifugal pump, passed through a heater and liming trough, returned to the top of the diffuser, and then percolates the bagasse. In this way defecation is effected. The bagasse is afterwards exhausted systematically as in ordinary diffusion. The juice having parted with its impurities to the bagasse is ready for evaporation.

The Harvey firm have installed Naudet plants, and Mr Harvey * reports that an extraction of 95 per cent. has been obtained in Madeira, whilst in Porto Rico 96 per cent. sucrose was recovered with a 9 per cent. dilution in 100 of cane (equal to about 10 per cent. in 100 of juice), the syrup having 1.3° Brix [total solid] less than dry milled juice, and the same quotient of purity.

The **composition of cane juice** varies. The following figures extracted from Prinsen Geerligs' "Cane Sugar" will serve to give an idea as to its components. It will be observed that reducing or invert sugar is the constituent which mainly distinguishes cane from beet juice.

The figures display in a clear fashion how glucose, being more diffusible, is expressed more in the first mill, whereas the colloidal pectins and albumens are expressed more completely in the second and third. As regards the maceration juices, these, if reduced by calculation to original gravity, show similar compositions to those got by expression without maceration.

* *International Sugar Journal*, 1905, 326.

	Black Java Cane without Maceration.			Borneo Cane with Maceration.		
	First Mill.	Second Mill.	Third Mill.	First Mill.	Second Mill. Diluted Juice.	Third Mill. Diluted Juice.
° Brix	19.2	19.3	19.0	18.5	14.8	6.7
Sucrose	16.49	16.33	15.95	16.76	12.65	5.50
Reducing sugar	1.98	1.57	1.52	0.89	0.59	0.33
Ash	0.28	0.41	0.42	0.244	0.425	0.199
Gum and pectin	0.125	0.376	1.250	0.063	0.150	0.099
Albumen	0.025	0.092	0.054	0.024	0.068	0.047
Free acid	0.048	0.072	0.096	0.042	0.039	0.016
Quotient of purity*	85.9	84.4	84.0	90.59	85.47	82.10
Glucose ratio†	12.0	9.6	9.5	5.3	4.7	6.0

The **clarification of cane juice** is still largely performed by the old style process of defecation with lime, although carbonation and sulphitation are extensively employed, on the same general principles as with beet. But by reason of the relatively large amount of C_6 sugar great care has to be exercised on account of the decomposition of these by lime into organic acids, which may cause injury. Thus in carbonation a temperature greatly exceeding 50° is not advisable.

In event of the juice being infected with organisms it may be heated to sterility before liming.

In the practice of defecation everything depends on the use of the correct proportion of lime, and the "tempering" ought to aim at neutralising the free acids. The lime salts precipitated on heating absorb or mechanically withdraw most of the albumen and pectin and remove fibrous particles, the whole rising to a scum on the top of the pans.

Defecators consist of hemispherical steam-jacketed copper pans. After heating nearly to boiling the mass is allowed to subside, and there is tapped off from below first the heavier sediment, sand, etc., then the clear juice, and finally the scum.

As variations of this procedure the juice may be boiled in iron pans and drawn off, when, as air has been expelled, the scum sinks in the settling tanks; or the scum is removed by skimmers into a gutter at the top of the tank; or in continuous defecation the juice at about 90° passes through one or more pans, in which it is rapidly boiled, continuously to the settling tanks.

In Denning's system the limed juice is pumped through three horizontal vessels having pipes connected with chambers at each end, so that the juice rapidly traverses them backwards and forwards. In the first vessel, or "absorber," cold juice circulates outside the pipes, and passes on to the second absorber, where it circulates inside the pipes, which are heated by exhaust steam. In the third, or "digester," the juice is rapidly brought to about 110° C. by circulation in the pipes surrounded by live steam. The hot liquor then passes through the pipes of the first absorber, thus saving heat by a preliminary warming of the contents of that vessel.

Concentration to Thick Syrup.—This used to be done in open pans over free fires, a process which tends to the formation of caramel and invert sugar, and which was most wasteful of fuel. Heating by means of steam coils was next adopted, a process ultimately supplanted by "multiple-effect" evaporation introduced by Rillieux and modified by Jelinek. In principle the process is simple. Steam from a closed juice evaporator is caused to heat a second at lower temperature, which in its turn heats a third in triple-effect working; or a fourth and sometimes a fifth vessel may be added in quadruple and quintuple effect (Fig. 59). The last vessel is in connection with an exhaust pump, whereby steam is removed and pressure reduced, so that boiling takes place at a lower temperature, with the result that very little heat is lost. The syrup passes from the first vessel onward with increasing concentration, and under diminishing pressure.

Two main types of evaporators are in use having vertical and horizontal heating respectively. In the vertical type the apparatus (see Fig. 63) consists of a tall cylinder having at the bottom the heating space, which is made up of two horizontal iron plates perforated and fitted with two hundred

* Percentage sugar in total solids. † Glucose per 100 parts sucrose.

to three hundred brass or copper pipes of about 30-55 mm. diameter and several wider circulation tubes. The whole forms a steam chest in which the outsides of the tubes are heated either by direct steam at 1½ atmospheres (112° C.) in the first unit, or in subsequent units by vapour from the preceding units. The juice admitted below at about 75° C. is raised to boiling on entering the tubes, is forced up the narrow tubes, and down by the wider "circulators." The juice level ought to be such that on ebullition the froth overflows the top of the heating chamber. Concentrated juice passes from a valve in the bottom to the next unit. Disengaged air and ammonia pass off through a special tube. The steam from the boiling juice is deprived of sugar conveyed over by spirting by a dephlegmator in the upper dome and by inclined baffle plates in the horizontal drum connected therewith, whence the syrup returns to the evaporating space. The vessel is further fitted with observation windows, syrup level, and hydrometer test glass, manometer and thermometer.

In the **horizontal** or **Wellner-Jelinek** plant the steam traverses layers of horizontal tubes surrounded by the juice and passes backwards and forwards through the layers of tubes.

The vapours from the last unit are removed by **barometric water pumps**, where the steam is condensed by a spray of injected cold water, and the condensed water falls through a height of more than 30 ft., air being withdrawn by air pumps (Fig. 60).

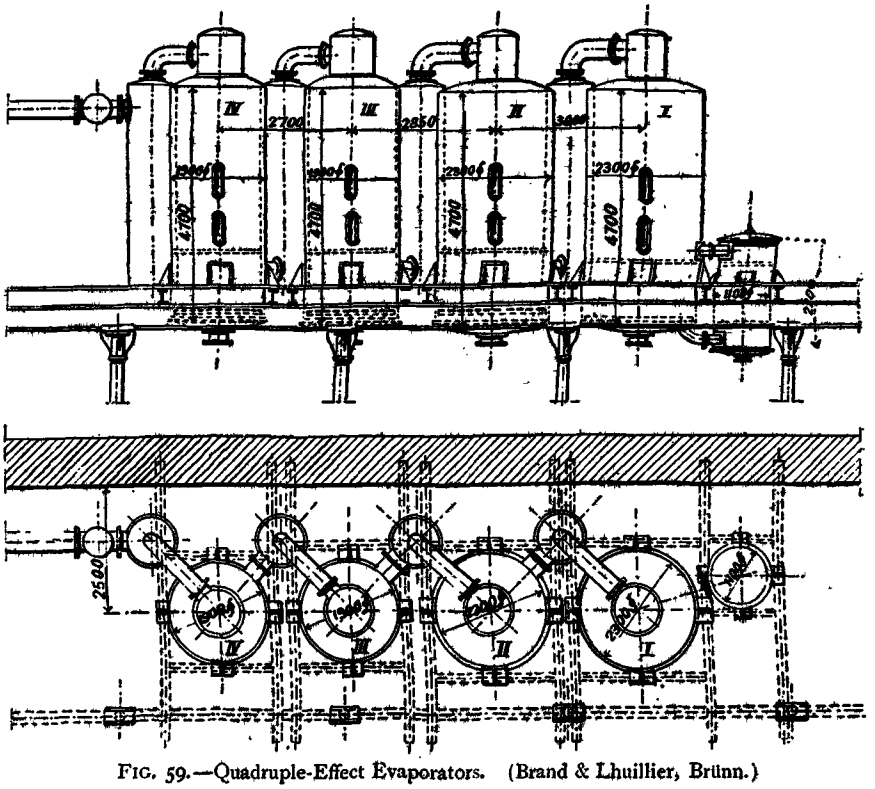


FIG. 59.—Quadruple-Effect Evaporators. (Brand & Lhuillier, Brünn.)

Concentration is carried on to about 60° Balling for beet juice or 60 per cent. Brix for cane, and the quantity of water to be evaporated (W) may be calculated from the formula—

$$W = K\left(1 - \frac{S_1}{S_2}\right),$$

where K = weight of juice and S_1 and S_2 initial and final gravities respectively.

Using steam at 1.5 atmospheres in the first unit, we have a temperature of 112° C., and if we have 60° as the boiling point in the last unit, the total fall is 52°, which is divided in multiple effect between the various units. Thus the temperature difference, *i.e.*, the difference between heating and evaporated steam, in each unit will be $\frac{52}{n}$, where n is the number of units. This fall is, however, not equal in practice, rising from the first to the last vessel.

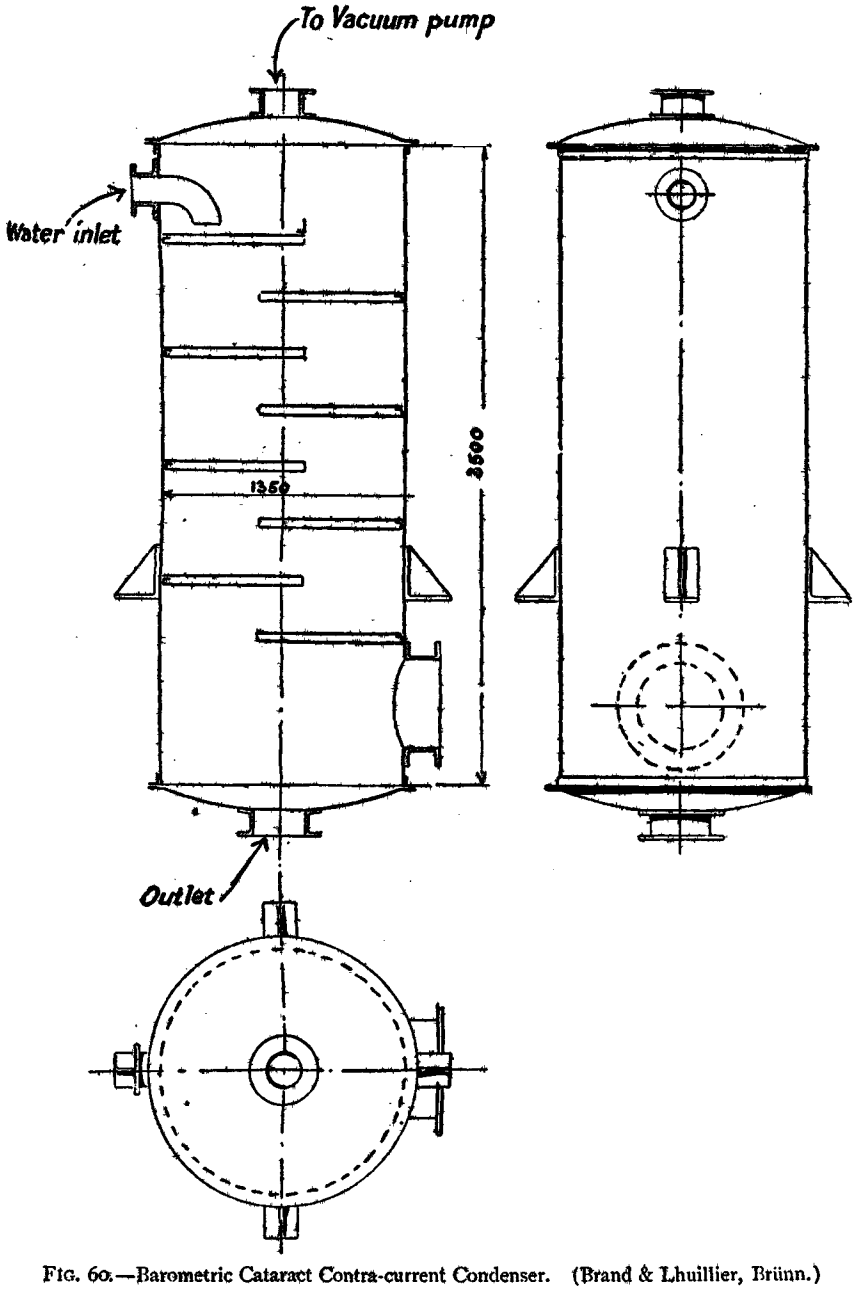


FIG. 60.—Barometric Cataract Contra-current Condenser. (Brand & Lhuillier, Brünn.)

Some data illustrating the process of multiple-effect evaporation, extracted from figures given by Jelinek for the horizontal system, are here tabulated.

It will be seen that the gain by adding units diminishes, and in practice generally triple and never higher than quintuple effect is used. The efficiency depends on the "coefficient of transmission," *i.e.*, the calories transmitted per minute per square metre of heating surface for 1° C. difference. For the horizontal system this has been ascertained at 22, for the upright at 15.

	Simple Effect.	Double Effect.		Triple Effect.			Quadruple Effect.				Quintuple Effect.				
		I.	II.	I.	II.	III.	I.	II.	III.	IV.	I.	II.	III.	IV.	V.
Temperature of heating steam -	112	112	86	112	94.6	77.4	112	99	86	73	112	101.6	91.2	80.8	70.4
Temperature of boiling juice -	60	86	60	94.6	77.4	60	99	86	73	60	101.6	91.2	80.8	70.4	60
Pressure in millimetres- - -	152	456	152	648	318	152	733	460	266	152	804	553	367	239	152
Kilos steam condensed per hour per square metre	129.7	64.98	61.50	43.35	40.81	41.16	32.52	30.54	30.73	30.92	26.01	24.4	24.51	24.6	24.73
Kilos water evaporated per hour per square metre	124.8	61.50	62.28	40.81	41.16	41.52	30.54	30.73	30.92	31.11	24.4	24.51	24.6	24.73	24.74
1 kilo steam entering first vessel evaporates kilos water	0.9	1.96		2.85			3.79				4.72				
Kilos steam required to evaporate 100 kilos water	111.11	51.3		35.08			26.38				21.18				

The saving in fuel achieved by multiple-effect evaporation is very great, about 80 kilos coal being required per ton of roots as against about 400 in the days of direct fire heating. It is a point, moreover, of special significance to the cane industry, which depends on exhausted cane or "megass" for its fuel.

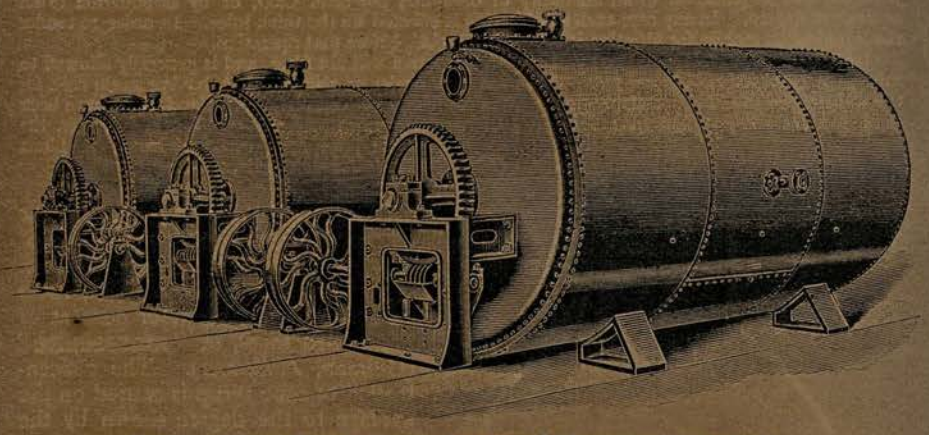


FIG. 61.—Closed Type Massecuite Receivers for Crystallisation in Motion.
(A. & P. W. M'Onie, Glasgow.)

During heating in evaporation there occurs with beet juice a notable decrease in alkalinity. This is due mainly to the disengagement of ammonia.

Juice of 12° Bg. usually has a phenolphthalein alkalinity of 0.015-0.02 per cent. reckoned as CaO, and on concentration to 60° Bg., instead of giving five times, it

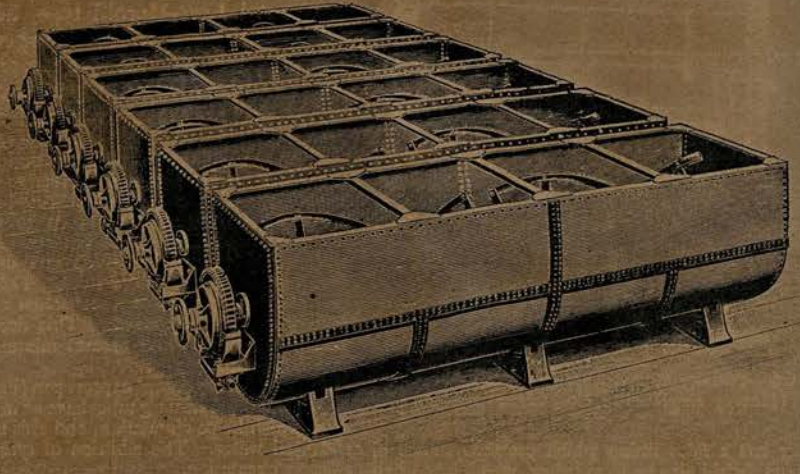


FIG. 62.—Open Type Massecuite Receivers for Crystallisation in Motion.
(A. & P. W. M'Onie, Glasgow.)

gives only about three times this value. Occasionally the decrease causes very bad boiling and discoloration, and may be corrected by addition of soda. Further, lime salts tend to separate on concentration, and form incrustations which seriously impair the efficiency of the plant. This may be overcome by promoting rapid circulation of the juice as in the special arrangement of the heating chest or

calandria in the evaporators made by the Harvey Engineering Company of Glasgow (Fig. 63).

In many cases in the beet works the so-called middle juice, *i.e.*, juice from the last evaporator but one, of sp. gr. 30°-35° Bg., is saturated before further evaporation. This is done by joint carbonation and sulphitation to an alkalinity of 0.02-0.04 per cent. CaO, or by sulphitation to an equivalent degree. In any case such sulphitation is effected on the thick juice. In order to render the liquid more mobile for filtration it is raised to 95° C. before that operation.

Juice from cane which has been purified by defecation will not filter, and is generally allowed to subside in eliminators at below 70°. These are rectangular or circular pans, having steam coils for the warming of the fluid. Sulphitation is often combined with elimination. Sand filters have been tried and are efficient, but have the defect of requiring much wash water. When, however, the cane juice has been carbonated it filters easily through ordinary filters.

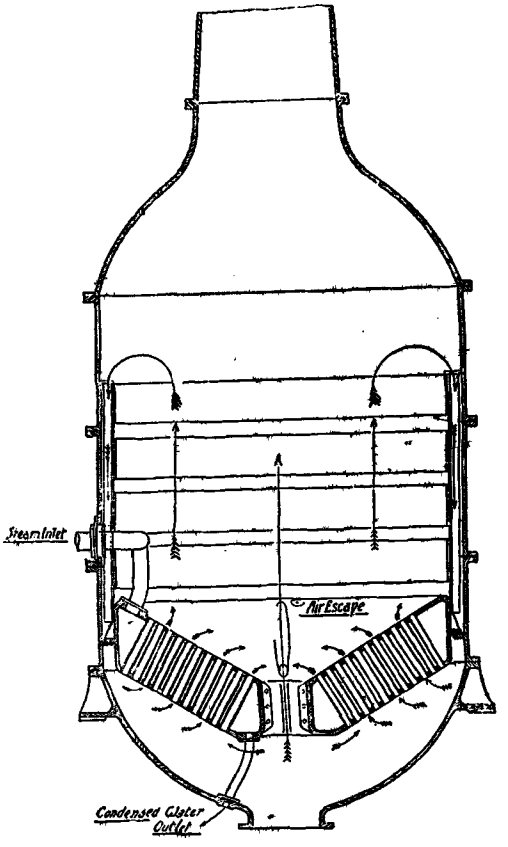


FIG. 63.—Harvey Patent Express Vacuum Pans. (Harvey Engineering Co., Glasgow.)

Boiling to Crystallisation, or Strike Point.—Beet syrup of 60° Bg. is in this stage boiled to from 3.5-7 per cent. water content, these values showing the water content of the boiled mass, or "**massecuite**" (German, *Füllmasse*). The concentration of cane syrup is carried on the average to the degree shown by the composition :—

Sucrose	81.10
Glucose	6.93
Ash	1.12
Water	8.66

Boiling is effected in vacuum pans which in Austria are generally of the horizontal Lexa-Herold type, heated by brass steam tubes arranged in sections, which can be separately heated. Upright strike pans are also in use, and are general in cane boiling.

The principles governing the working of a vacuum strike pan are similar to those pertaining to the multiple-effect boilers. Steps must, however, be taken to secure effective circulation, which is more difficult with the thick mass of syrup and crystals than with the concentrated juice. This may be done by injection at the bottom of the boiling mass of dry steam. This does not impair the vacuum and secures mixture and steady boiling.

In the Harvey patent express pan (Fig. 63) the calandrias or heating tubes have an inclination which helps circulation, and this model further has a false lining which prevents return of condensed water. The addition of syrups or molasses should also be from below, which again helps effective circulation.

The process of boiling falls into well-defined stages. At first we have concentration to thick syrup of about 80°. Then follows boiling to "grain," a most important stage, having for its object the formation of uniform crystals of such size as not to pass through or clog the meshes of the centrifugals. The supersaturated syrup is generally caused to grain or crystallise spontaneously, or by admission of fresh juice, which by promoting circulation, and still more by depressing the boiling temperature, induces rapid crystallisation in fine grains. The subsequent boiling has in view the growth of the already formed crystals and solution of the very fine

ones, and care is exercised to secure that a fresh small crystal formation or "false grain" shall not occur. Boiling is continued to a water content of 3.5-4 per cent. or 6-7 per cent., according as it is intended to cool at rest or in motion. The massecuite is discharged either into ordinary coolers or into special vessels designed for the very generally practised "**crystallisation in motion.**"

The crystallisers may be open or closed cylindrical vessels, and may or may not be jacketed for warm or cold water. They have shafts with blades, whose rotation keeps the mass in constant gentle motion. This has the effect of causing the sugar separated on further cooling from the warm saturated solution to be deposited on the existing crystals, and not in the form of false grain throughout the mother liquor.

The very great solubility of sucrose will make it clear that the problem of a maximum crystallisation is one of great practical difficulty, having in mind the necessity of removing the molasses mother liquors which entangle the grain. Moreover the molasses contain uncrystallisable sugar held in solution by the salts on account of their so-called "**melassigenic power.**" (See pp. 142, 143.)

Geerligs defines **molasses** as: "A hydrated combination between sugar and salts, which cannot be broken up by dissociation in a concentrated state, and therefore cannot yield sucrose in a crystallised form." **Cane molasses** contains about 55 per cent. sugars (sucrose + invert), 20 per cent. water, and 9 per cent. ash.

Beet molasses contains about 50 of sugar, 10 of salts, 20 of water, 10 of nitrogenous and 10 of non-nitrogenous substances.

To facilitate **curing** or **centrifuging**, green molasses may be added to the massecuite, which will give sufficient mother liquor to secure the necessary mobility. Such added syrup will be recovered plus that due to the fresh massecuite, and is boiled down from time to time to sugar and exhausted molasses.

The "**absolute recovery**" method is of great value and interest, and an account condensed from Prinsen Geerligs is here given. The relation between the purity of the massecuite and the corresponding molasses cured hot is given by Pasma as:—

Massecuite of	90	purity	yields molasses of	75	quotient.
,,	88	,,	,,	71	,,
,,	85	,,	,,	65	,,
,,	82	,,	,,	62	,,
,,	80	,,	,,	60	,,
,,	70	,,	,,	50	,,
,,	65	,,	,,	45	,,

If the syrup is over 80 purity it is reduced thereto by addition of green molasses of 60 purity, which will, as seen, again yield 60 molasses. On curing hot, first sugar and 58-60 molasses result. Sufficient of this molasses is then drawn into a second massecuite as to give a purity of 70, and this on boiling and hot curing yields first sugar and 48-50 molasses, which finally is used to reduce an 80 massecuite to 60, when, on high concentration and cooling, sugar and exhausted molasses result.

Curing or separation of crystals from the magma of crystals and molasses is effected in turbines.

Those of the Weston type are most usual. The spindle is suspended and driven from above by water turbine, or belt, or electrically, the power being applied accurately at the point of suspension. Vibration is reduced to a minimum by the conoidal rubber buffer, and discharge is effected below—a great saving in time and cleanliness. (Figs. 64, 65.) The turbines make about 850 revolutions per minute, and may be arranged for continuous work.

From crystallisation in motion the viscid massecuite is turbined direct. If cooling has been done in tanks the hard massecuite is broken up in pug mills, and incorporated with the requisite molasses.

Turbining fails to absolutely separate the adherent molasses from the crystals, and these, therefore, are washed or "purged." This may be done by injecting a fine spray of water into the revolving machine, after the molasses has passed off, or by means of a jet of steam and air. The cleansing syrups inevitably dissolve some sugar, and are therefore collected apart from the molasses. Obviously, a pure concentrated sugar solution will be as effective to remove salts and non-sugars as water.

The product is usually machine dried in long inclined cylinders having scoops whereby the moist mass is turned over by the revolutions and meets a current of warm air, entering at about 120° and leaving at about 50°. Sometimes the sugar is dried by means of dry steam in the turbines.

Although pure sugar is not hygroscopic, there is often a coating of molasses which absorbs water, and under favourable temperature conditions affords a good medium for the growth of moulds and yeasts, whereby inversion and deterioration

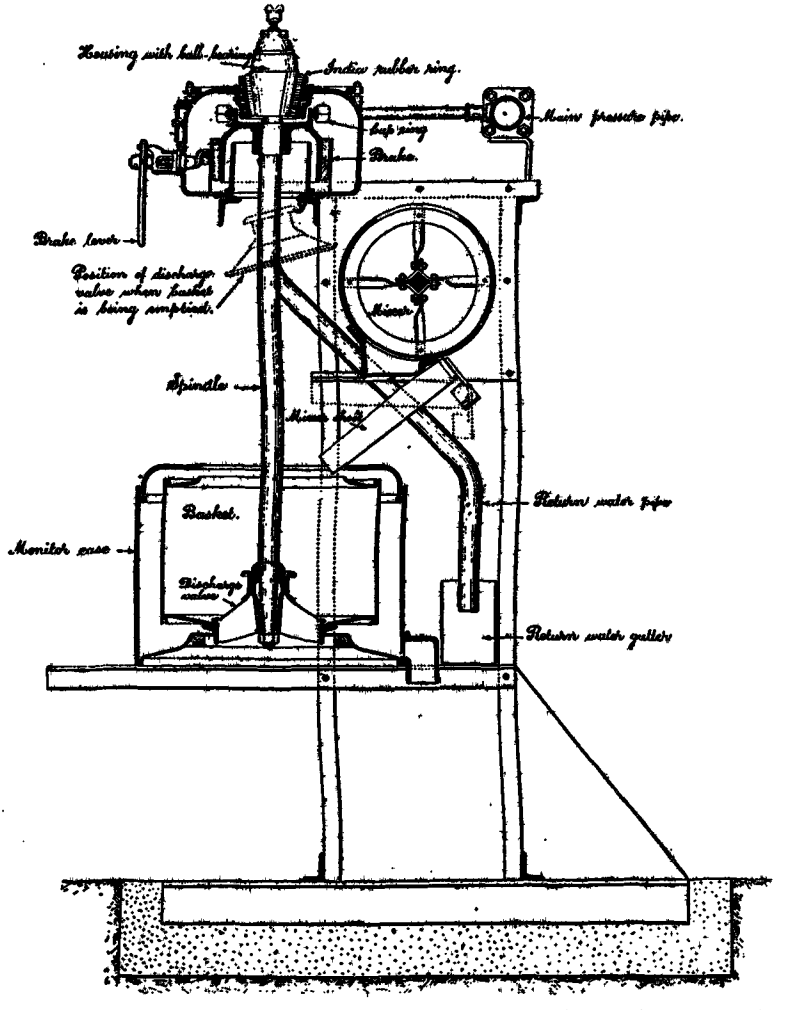


FIG. 64.—Patent Water-driven "Weston" Centrifugal Machine, showing Patent Steel Frame. (Messrs Watson & Laidlaw, Glasgow.)

is caused. In the case of cane sugar the presence of invert in the product and the warm moist climate render the material very prone to these changes. Close packing in bags of the dry cool product in stores capable of regulated ventilation or closing according to the hygrometric state of the atmosphere is recommended. Beet sugar is less liable to alteration, and is advantageously stored after artificial cooling. Alkalinity does not appear to be a certain safeguard, which is to be expected from the circumstance that alkaline media are most favourable to bacterial growth.

As regards the composition of raw sugar this naturally varies, beet being distinguished from cane by freedom from invert sugar. In the **commercial valuation** the polarisation *minus* ash × 5 *minus* invert is the basis for cane. For example, a sugar having 97.0° polarisation, 0.85 reducing sugar, and 1.10 ash, has the value 97.0 − 0.85 − 1.10 × 5 = 90.65. A beet sugar having 94.95° polarisation, 1.04 per cent. ash, and 1.89 per cent. organic non-sugar, would have the value 94.95 − 1.04 × 5 = 89.75, on the generally accepted standard that 1 part of mineral matter prevents the crystallisation of 5 parts of sucrose. Alternatively, beet is sometimes valued by deducting 2.25 times the joint ash and organic non-sugar; thus in the above case 94.95 − (1.04 + 1.89) × 2.25 = 88.36.

The final **exhausted syrups** or mother liquors form the **molasses**, the composition of which has been previously indicated. This was once an irksome bye-product, but to-day is used for various purposes, *e.g.*, in spirit manufacture, for instance West Indian rum; for making alcohol from beet molasses, (p. 293); for making trimethylamine (p. 376); for extraction of a further yield of sugar; for making cattle food preparations; or for direct feeding to the animals. Refined syrups, after inversion and clarification, form the **treacles** or **golden syrups** of consumption. Beet molasses is less pleasantly flavoured and more highly charged with salts. It is fed to the extent of about 30 per cent. to cattle in Germany and Austria, in rations of from 2 to 6 kilos per 1,000 of body weight per day, generally and advisedly in admixture with other foods or neutral bases such as peat. In England a mixture of molasses and peat moss is somewhat widely used under the name of "molassine meal." Owing to the high salt content irrational feeding with molasses is dangerous, causing digestive and urinary trouble, and animals need to be habituated to it by graded feeds. A similar preparation of cane molasses absorbed in the residual internal and finer fibre of the cane or bagasse is "molascuit." Both these are convenient and portable forms of food stuff.

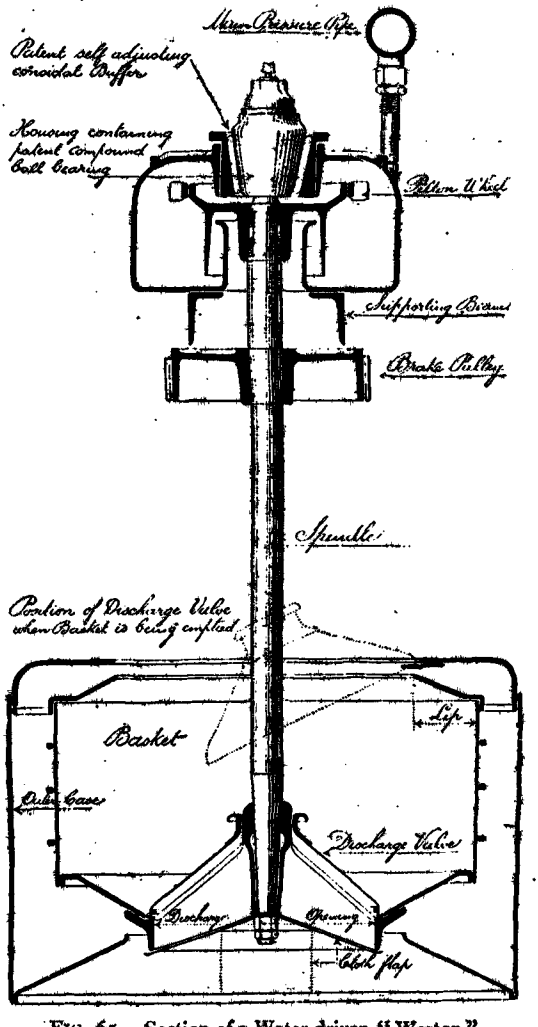


FIG. 65.—Section of a Water-driven "Weston" Centrifugal Machine.
(Messrs Watson & Laidlaw, Glasgow.)

Separation of Crystalline Sugar from Molasses.—Two main processes are available, viz., **osmosis**, and precipitation either of **strontium**, **or calcium sucrates**. The **osmotic process** depends on the circumstance that the salts diffuse more rapidly through parchment paper into water than does the sucrose. In this way a partial separation is possible, incomplete, since obviously sucrose also will diffuse, though less rapidly.

The general arrangement of an osmosis plant is that of parallel flat chambers separated by

parchment paper, in which flow molasses and water in alternate chambers and opposite directions. The osmosed molasses is boiled to grain, and the resultant syrup re-osmosed until a final residual molasses which would not repay further osmosis is obtained. The osmosis water may be used as a fertiliser, or worked for spirit or potash. On 100 of molasses of 78° Balling about 15 per cent. of sugar may be recovered, having a quotient of about 95.

The separation by means of **strontia** depends on the formation of the sparingly soluble basic sucrate $C_{12}H_{22}O_{11},2SrO$. In this process molasses and strontium hydroxide solution—eventually solid strontia—are boiled to an alkalinity of about 15-20 per cent. $Sr(OH)_2$, reckoned on the basis of 1 part sucrose to 2.5 parts crystallised $Sr(OH)_2$. The precipitate is rapidly filtered and washed with hot 12-14 per cent. strontia solution. On leaving at a low temperature (- 10° C.) with a 2 per cent. $Sr(OH)_2$ solution, the basic saccharate separates into crystalline hydroxide, and the sugar with half the strontia passes into solution. After separation the solution is saturated, and the sugar evaporated to massecuite. Strontium carbonate, and that recovered from the mother liquors, is reburnt, and the clarified mother liquors, after separation of strontia by carbon dioxide, are evaporated and burnt for potash.

In **Steffen's lime process** the sugar is precipitated by means of thorough agitation at not above 20° C. with finely powdered well-burned quicklime, as tribasic sucrate, which is used as a lime substitute in the treatment of diffusion juice.

Refining.—The technique of sugar refining varies according to the quality of the raw sugar, and the nature of the trade article which it is desired to turn out.

Raw cane or beet, or blends of both, may be operated upon, it having been claimed that the alkalinity of beet may correct the occasional acidity of cane.

On entering the refinery the raw sugar is sampled and stored, *e.g.*, in large bins, until required.

A preliminary curing in the turbine is sometimes resorted to, in the so-called *affination* process, and affination sugar is often used as an article of consumption, but naturally not of the first class. This treatment has the object of removing adherent impure syrup, which envelops the grain, and may be very dark coloured. In this syrup, obviously, the greater part of the non-crystallisable sugar and mineral matter is concentrated. The consistency of some raw cane, or muscovado, sugars does not permit of affination. When affination is feasible, the raw material is thinned by incorporation with a syrup of such strength as not to dissolve the crystals, but to merely act as a diluent of the adherent syrup. The mass is then turbined, either in ordinary turbines (*q.v.*) or in open bottomed machines, in which an inverted cone on the spindle directs the magma, by centrifugal force, on to the basket of the turbine, where the same force holds it during spinning and purging, and on stopping the machine the sugar falls out by gravity, without handling.

It is dissolved, in blow-up pans, in such fashion as to give a solution of approximately 2 parts sucrose to 1 part water, and at this stage separated from coarser adventitious impurities.

The further purification consists in a preliminary treatment and a bone-charcoal filtration. Formerly bullock's blood was added, and occasionally lime is used. Apart from mere neutralisation this stage of the work, whatever may be the special treatment selected, has in view the formation of a voluminous precipitate, which will carry down by absorption gummy and protein impurities, on the principles observed in the carbonation process.

As substitutes for the old-fashioned blood or albumen treatment, a mixture of aluminium sulphate and superphosphate has been tried, but not with advantage, owing to the solubility of the gypsum and the occurrence of free sulphuric acid in the superphosphate; or, again, baryta may be used, but this is not considered advisable, since the soluble barium salts are poisonous.

After either filter-pressing, or filtration through bag filters, the clear juice is passed through the bone char filters.

No substitute for bone charcoal is so far available. In spite of the small percentage of carbon in bone char and the well-known gas absorptive power of vegetable charcoal, the latter does

not possess in any degree the powerful decolourising effect of bone char, nor does it lend itself satisfactorily to revivification.

New animal charcoal contains from about 8·13 per cent. of carbon, 78.5-84 per cent. of calcium phosphate, 7.5-9 per cent. of calcium carbonate, and small quantities of alkalis, iron, and silica. The carbon of fresh char always contains fixed nitrogen and a little hydrogen, the former amounting to about one-twentieth of the total carbonaceous matter, and diminishing on repeated reburning. It is possible that the nitrogenous matter plays an important part in the special decolourising action, which is not understood. It is, however, known that pure vegetable charcoal does not possess this property in the same degree, though bone char freed by means of acid from calcium salts is very efficient. Traces of ammonia and of calcium sulphide may be present, which are obnoxious, and are to be got rid off by washing and reburning.

The **char filters** have commonly the form of iron cylinders of varying dimensions, which may hold upwards of 20 tons of char, the grain of which is also

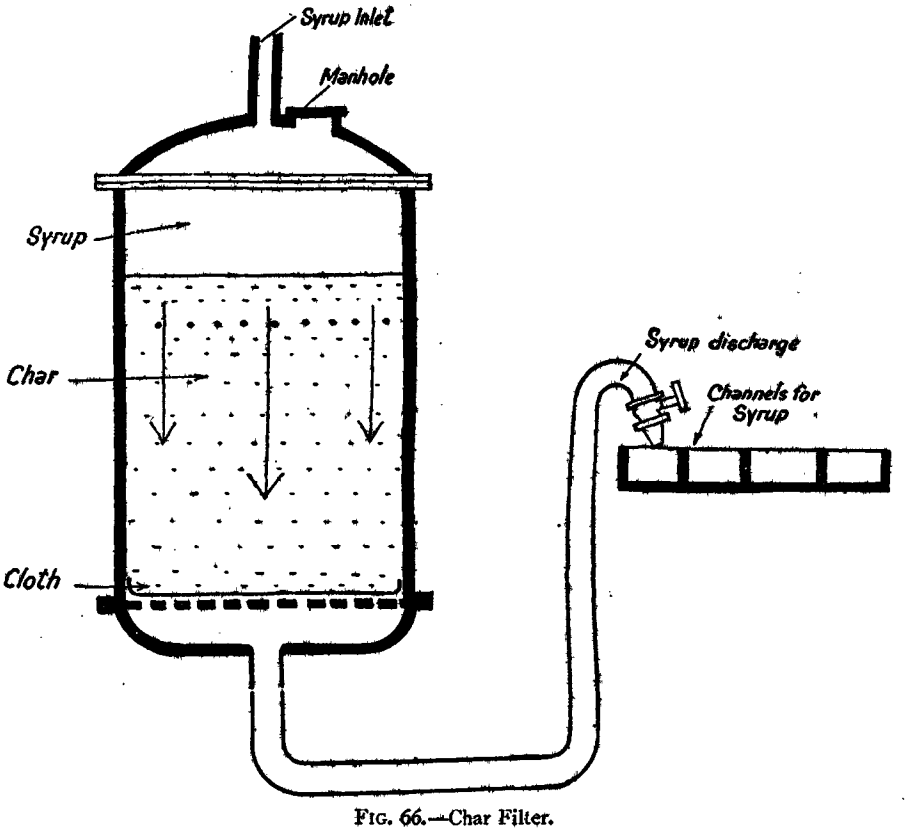


FIG. 66.—Char Filter.

very variable, a 20/30 sieve size being not uncommon The char is uniformly packed on the filter cloth (see Fig. 66), and the solution passes evenly through the mass, at a temperature of 68°-70° C., is drawn off, as shown, and the filtrate collected, according to colour, in channels or gutters. At first water white, the filtering syrup eventually becomes yellow, at which point the char is thoroughly washed till free of sugar, and then copiously with water to remove soluble impurities absorbed from the sugar solution, dried, and reburnt.

The **charcoal kilns** usually consist of oval pipes arranged vertically in a furnace in three rows on each side. The char, entering from above, is thus submitted to strong heat or dry distillation, whereby the organic impurities are expelled without loss of carbon. It passes downwards at a speed, capable of regulation by the discharge valves, depending on the temperature of the furnace and the

order of proximity of the row of pipes to the fire. The pipes are continued downwards through the kiln floor, and thus serve as air coolers, whereby loss of carbon by ignition on emerging from the pipes is prevented. The effective life of the char is long, and may extend over several years.

The art of **sugar boiling** in refinery work reaches a very high level, demanding a long apprenticeship. The object is to obtain a uniform grain of a size governed by the nature of the desired finished article, and the boiling is done in vacuum pans (*vide supra*). Having obtained a crystallisation, or grain, great care is required in the introduction of fresh syrup, to ensure that the number of crystals shall not increase, but that those first formed shall grow in size, and that fresh crystal formation or "false grain" shall not occur. False grain formation is especially objectionable in boiling lower massecuites, for its appearance very much interferes with the turbining of the crystals from the surrounding molasses.

When boiling has reached the required point the product may be directly turbined, or further crystallised in motion, in which the existing crystals grow at the expense of the sugar of the cooling saturated mother liquor.

Granulated Sugar is prepared by passing the turbined and washed wet product through granulators, long revolving cylinders, inclined at about 20°, in which the mass is propelled and disintegrated by revolving arms. In the reverse direction there passes a current of warm air to dry the crystals, which are then sieved on vibrating tables, or other types of mechanical sieve.

For the manufacture of **cube or "loaf" sugar**, so named from the now obsolete loaves or cones into which sugar was formerly moulded, is in many modern works prepared by special processes, of which the Adant may serve as an illustration. A series of detachable iron frames is built up so as to form rectangular moulds about 1 in. thick, arranged radially around the periphery of a hollow cylinder, which is then placed into a well-fitting containing ring. Massecuite, discharged into a heated reservoir vessel, is then run in until the moulds are full. After cooling, the moulds have the consistency of a dense mass of crystals in a thick syrup, and the inner ring is detached, by the aid of a compressed air blast; and transferred to a centrifugal of heavy type. Therein the sugar is freed, *in situ*, from syrup, and washed. On taking the form to pieces, complete rectangular slightly wedge-shaped tablets result, which after drying are machine-cut to the form of cubes or otherwise as may be desired.

We are indebted for diagrams, and desire to express our thanks therefor, to the following firms:—

Actien Gesellschaft für Maschinenbau, vormals Brand & Lhuillier, Brünn, Austria; Maschinenfabrik Büttner, Verdingen am Niederrhein, Germany; The Harvey Engineering Company, Glasgow; Messrs A. & P. W. M'Onie, Glasgow; Messrs Watson & Laidlaw, Glasgow.

Glucose, Dextrose, or Starch Sugar

Glucose, $C_6H_{12}O_6$, forms the crystalline hydrate, $C_6H_{12}O_6H_2O$, which melts at 86° C. and of which 97.8 parts are dissolved by 100 of water at 15° C. It is very soluble in methyl alcohol. Glucose displays multarotation, a freshly prepared cold solution having $[\alpha]_D + 105$, which decreases rapidly on heating to the final equilibrium value + 52.85.

Alkalis isomerise glucose, yielding an equilibrium mixture of glucose, fructose, and a little mannose, also produced similarly from fructose, but alkalis at the same time break down glucose, yielding complex organic acid salts.

Glucose is oxidised by Fehling's solution, as also are maltose and fructose; yields an osazone (M.P. 205°) also given by mannose and fructose; and with α-naphthol and sulphuric acid gives a red colour, a reaction which is not characteristic, being given also by sucrose and other sugars.

Manufacture.—Commercially glucose is manufactured from starch by heating with dilute mineral acids, when hydrolysis ensues:—

$$(C_6H_{10}O_5)_n + nH_2O = n.C_6H_{12}O_6.$$

Mixed with a large amount of dextrine it comes into commerce: (1) as solid glucose, (2) as the viscid syrup known as "starch syrup."

The industry is of Continental origin and dates from the time when cane sugar was excessively dear, so that efforts to produce a substitute from starch had some possibility of success. At the present time, however, glucose is valued not as a substitute for sucrose but rather for the presence of certain dextrines in the commercial product, which are: (1) valuable food stuffs, (2) are soluble, (3) will not crystallise, (4) are non-fermentable. Such glucose is largely used: (1) as a malt substitute in brewing: the dextrose ferments to alcohol, and the unfermentable dextrines increase the percentage of extract in the beer; (2) for the manufacture of glassy sweets, cane sugar being unsuitable for the purpose; (3) for adding to honey; (4) for use in confectionery, cakes, preserves, jams, jellies, syrups, etc.

The great drawback to the use of glucose is its want of sweetness, being only two-thirds as sweet as sucrose. The addition of saccharin or other artificial sweetener is illegal in some countries.

The hydrolysis of starch by dilute acids is a complex change (see Starch), the starch first breaking down into dextrines which then break down into maltose, and this finally into dextrose. The saccharification only proceeds easily in very dilute solutions, as shown in the following scheme:—

$$\underset{\text{Starch.}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{Dextrines.}}{(C_6H_{10}O_5)_n H_2O} \longrightarrow \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Dextrose.}}{2.C_6H_{12}O_6}$$

In practice, the starch is intentionally left incompletely hydrolised, the presence of dextrines being essential. Moreover, in the concentrated solution some of the dextrose molecules condense together to produce gummy dextrine-like products called "glucosines." Simultaneously a certain amount of "isomaltose," $C_{12}H_{22}O_{11}$, a sugar isomeric with maltose, but not fermentable by yeast or hydrolysable by enzymes, is also produced. The rate of hydrolysis of the different acids varies considerably, the stronger acids having a more rapid action than the weaker; thus, taking the hydrolysing power of an equivalent weight (36.5 g.) of HCl as 100, the following table expresses the hydrolysing power of the *equivalent weights* of some other common acids:—

Acid.	Equivalent Weight.	Hydrolysing Power.
Hydrochloric acid, HCl	36.5 g.	100
Sulphuric acid, H_2SO_4	49 g.	70
Nitric acid, HNO_3	63 g.	100
Tartaric acid, $C_4H_6O_6$	150 g.	2.5
Formic acid, H.COOH	46 g.	1.6

The starch is placed in a boiler, a small percentage (say ¼ per cent. or even less) of HCl or H_2SO_4 or HF is added and the whole heated under 1-2 atmospheres pressure, cooled, and the acid neutralised. If HCl is employed it is neutralised with Na_2CO_3, the small percentage of NaCl produced being imperceptible to the taste; H_2SO_4 is neutralised with $CaCO_3$, the $CaSO_4$ produced coming down as a precipitate. HF is completely precipitated as CaF_2.

Starch Syrups.—Moist potato-starch, carefully purified from nitrogenous matter (the presence of which yields a dark product), is used. 200 parts of water and as much H_2SO_4 as serves to make a 0.3 per cent. solution are placed in a boiler, and 100 parts of the starch (weighed dry) made into a milk with water are run into the boiling acid, so that the starch is almost immediately gelatinised. The mixture is then heated in a copper autoclave for one hour under 1 atmosphere pressure, so that about a half of the starch is hydrolysed to dextrine and the rest to dextrose (or maltose). The process is ended when a test portion gives no coloration with iodine—showing that all the starch has disappeared. The product is a non-crystallisable syrup having a density of 17° Bé. = about 30 per cent. of carbohydrate. The sulphuric acid is neutralised with $CaCO_3$, the solution filtered from the $CaSO_4$ through a filter-press, evaporated to 32° Bé. in a vacuum pan, again filtered from precipitated $CaSO_4$ through a filter press, and finally decolourised by filtering through animal charcoal, which simultaneously absorbs some of the finer particles of $CaSO_4$. The syrup is now again concentrated in vacuum pans to 42°-45° Bé. and should be clear and colourless.

A good concentrated syrup should be so viscid at ordinary temperatures that it scarcely flows; it should not become cloudy on standing and should bear a temperature of 140° C. without darkening in colour. The product, after heating to 140° and cooling, should solidify to a glassy mass, which is used for making sweets. It has only a moderate degree of sweetness.

Solid Glucose is manufactured in the same way as the syrup, but the hydrolysis in the autoclave is carried on for a longer time so that the resulting mixture contains almost twice as much dextrose as dextrine. The product, when filtered, decolourised and evaporated, solidifies as a white mass of microscopic crystals, in which fine needles of dextrose hydrate, $C_6H_{12}O_6.H_2O$, may be seen embedded in syrup. The crystalline dextrose hydrate, however, cannot be separated by ordinary means from the syrup. The following shows the composition of a starch syrup and of solid glucose thus manufactured :—

	Syrup.	Solid Glucose.
Dextrose	40·43 per cent.	55·61 per cent.
Dextrine	41·46 ,,	24·30 ,,
Water	15·19 ,,	15·20 ,,

A certain amount of "maltose" is always present. The maltose and dextrose together constitute the fermentable portions of the mass, the dextrines (which include isomaltose and glucosines) the non-fermentable portions.

It has not yet proved possible to manufacture pure dextrose on the industrial scale, since neither the crystals of the hydrate $C_6H_{12}O_6.H_2O$, nor those of the anhydride, can be easily centrifuged from the adhering syrup. Some American firms, however, evaporate the dextrose solution *in vacuo* until it is of the proper consistence; then crystals of pure dextrose, $C_6H_{12}O_6$, are stirred in, and the mass crystallises out as a mass of grains, which are then centrifuged and obtained in a colourless state. A very large amount of a dark-coloured syrup is produced in this process, which is sold to brewers for colouring porter, under the name "**Climax Sugar.**

Caramel, Burnt Sugar, Gravy Salt, Gravy Coleur, and Coleurs for Soups, Wine, Beer, Vinegar, Sauces, etc., are manufactured on a large scale from dextrose by making its solution alkaline with soda, evaporating, and heating to 220° C. The dark brown mass is poured into tins and allowed to solidify. Sometimes it is sold dissolved in a little water. Much used for colouring sweets, liquors, etc.

Asrylmusry gives the following recipe for making a **colour for rum** :—3 kilos of NaOH or KOH, 6 kilos water (or 4 kilos sodium or potassium carbonate and 8 kilos water) are dissolved by heating in a large iron pan, and then 120 kilos of glucose (or 130 kilos of syrup of glucose) are added, and the whole is heated over a direct fire until irritating vapours begin to be evolved. The heat is decreased, and the mixture stirred continually until the proper shade of colour is attained. 30 or 40 l. of water are then added in a fine jet. To produce a colour for **vinegar**, we take 6 kilos ammonium carbonate, 6 kilos of water, and 120 of glucose, and proceed as before.

Caramel from Cane or Ordinary Sugar.—The sugar is heated with continual stirring in an iron pan until the whole melts, turns brown, and suddenly begins to froth up. Not more than 15 per cent. of weight of sugar should be expelled, or the product will become insoluble. The change is stated to be represented by the equation :—$11C_{12}H_{22}O_{11} = C_{125}H_{188}O_{80} + 7CO_2 + 27H_2O$. Cane sugar caramel is an amorphous reddish brown brittle mass, M.P. 134°-136° C.; completely soluble in water, only partially so in alcohol. Bitter taste. Nonfermentable.

Invert Sugar and Honey; Laevulose

Invert Sugar is the mixture of glucose and fructose resulting from the hydrolysis of sucrose. It is manufactured from sucrose by heating in solution with small quantities of mineral acid. It is laevorotary, the laevo-rotation of fructose (laevulose) being greater than the dextro-rotation of glucose, and has $[\alpha]_D^t = -(27.9-0.32t)$, consequently, on inversion dextro-rotatory sucrose becomes laevo-rotatory. A mixture of laevulose and dextrose and a little sucrose occurs in the juices of many fruits—especially grape juice, which is quite free from sucrose. The mixture is

known as "grape sugar." Invert sugar, however, is never obtained commercially from plant juices after the manner of sucrose, because it is too soluble and too difficult to crystallise.

It is always manufactured by heating a 75-80 per cent. sucrose solution with a very small amount, say 0.02-0.05 per cent., of hydrochloric acid, or 0.2 per cent. of tartaric, citric, or formic acid, to 95°-100° C. and neutralising with soda. The resulting syrup must not be concentrated in the usual way or it browns, and consequently is sold as it stands. If it contains 75 per cent. or under of sugar it will not crystallise; syrups with 80 per cent. of sugar on cooling separate as a solid mass. This invert sugar is used for improving wine musts (see **Wine**); it is also used in making artificial honey, since it is chemically identical with honey, failing only the flavouring matters peculiar to that fluid.

Honey, in fact, is simply a mixture of dextrose and levulose, together with a little sucrose, dextrines, flavouring matters, pollen, and a little free formic acid, which acts as a preservative. In granular honey the crystals are of dextrose. When bees are fed on sucrose or glucose these materials pass over unchanged into the honey.

In making artificial honey, invert sugar prepared as above is mixed with about 25 per cent. of a natural honey, rich in flavouring matters.

Since the invert sugar contains sucrose, dextrose, levulose, and even dextrine, in amount almost the same as they occur in natural honey, the mixture has practically the same chemical and physical properties as real honey, and, in fact, cannot at the present time be distinguished from it. An adulteration of honey with dextrose from starch is easily detected, because of its strong dextrorotary properties.

Pure Levulose (fructose, fruit sugar) is obtainable from **inulin** — the laevo-rotatory starch of **Dahlia**, **Inula**, and **Chicory** — by heating with dilute acids in exactly the same way that dextrose is obtained from ordinary starch. Laevulose is sweeter than cane sugar, and is very soluble in water, but difficult to crystallise. It is easily decomposed by acids into non-crystallisable syrups. It reduces Fehling's solution very easily and ferments directly with yeast. It is strongly laevo-rotatory, the rotation being greatly effected by the concentration (c) of the solution and the temperature; $[\alpha]_D^{20} = -(91.90 + 0.111c)°$. Industrially laevulose is obtained from invert sugar by means of the difficultly soluble calcium laevulate. It could, however, be obtained on the large scale from **dahlias** (containing 12 per cent. inulin) or chicory.

Milk Sugar, Lactose, $C_{12}H_{22}O_{11}$, is manufactured from the whey left over during the manufacture of cheese. See under Milk, p. 78*a*.

Other Varieties of Sugar

Maple Sugar is obtained to the extent of 15,000 tons yearly in Canada and North America from the juice of the maple tree. In spring the mature trees (which may be 200 years old) can be made to yield sap containing about 2 kg. of sugar. The sap contains 2-4 per cent. of sugar, principally sucrose. It is consumed locally as a syrup. The industry is decaying, but maple sugar is highly valued for its flavour.

In the East Indies about 140,000 tons of sugar are made annually from the juice of the coco-palm and similar sugar palms. In Bengal great plantations of the palms exist, each palm yielding during the interval of twenty-five to thirty years about 38 kg. of sugar annually. The labour of cultivation is very small. The sugar is consumed locally.

Attempts to cultivate the **amber cane** (*Sorghum saccharatum*) in the United States for sugar have proved a failure, because besides sucrose the juice contains much invert sugar and non-saccharose constituents, so that it is difficult to get the sugar to crystallise out in sufficient quantity to repay working.

Estimation of Sugar

Glucose may be estimated volumetrically by titrating the boiling sugar with Fehling's solution ($CuSO_4 + KOH +$ Rochelle salt). The glucose reduces the copper, throwing down a red precipitate of cuprous oxide, the solution becoming decolourised.

Pavy's modification is easier. It consists in using a concentrated solution of ammonia with the Fehling's solution. The Cu_2O dissolves in this to form a colourless solution, and so does not interfere with the end point, but Pavy's method is usually confined to sugar estimation in fermented urine, which contains free ammonia.

Sucrose or cane sugar does not reduce Fehling's solution, but when hydrolysed by warming with dil. HCl it is converted into a mixture of dextrose and levulose (see **Invert Sugar**), which has the same reducing power as glucose—342 g. cane sugar = 360 g. invert sugar or glucose.

When the **cane sugar** solutions are fairly pure the amount of sugar is immediately given by the specific gravity with a floating hydrometer. The following gives the sp. gr. at 15° C.

Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.
0	1.00000	19	1.07907	38	1.16960	57	1.27297
1	1.00390	20	1.08354	39	1.17470	58	1.27879
2	1.00783	21	1.08804	40	1.17985	59	1.28465
3	1.01178	22	1.09257	41	1.18503	60	1.29056
4	1.01576	23	1.09713	42	1.19024	61	1.29650
5	1.01978	24	1.10173	43	1.19550	62	1.30248
6	1.02382	25	1.10635	44	1.20079	63	1.30850
7	1.02789	26	1.11101	45	1.20611	64	1.31457
8	1.03199	27	1.11571	46	1.21147	65	1.32067
9	1.03611	28	1.12044	47	1.21687	66	1.32682
10	1.04027	29	1.12520	48	1.22231	67	1.33301
11	1.04446	30	1.12999	49	1.22779	68	1.33923
12	1.04868	31	1.13482	50	1.23330	69	1.34550
13	1.05293	32	1.13969	51	1.23585	70	1.35182
14	1.05721	33	1.14458	52	1.24444	71	1.35817
15	1.06152	34	1.14952	53	1.25007	72	1.36457
16	1.06586	35	1.15448	54	1.25574	73	1.37101
17	1.07023	36	1.15949	55	1.26144	74	1.37749
18	1.07464	37	1.16452	56	1.26718	75	1.38401

A rapid way of estimating sugar is by the polariscope. The solution is clarified with aluminium sulphate or lead acetate, filtered, and its rotation taken in a 20 cm. tube. $[\alpha]_D^{20}$ for cane sugar = 66.4 (see p. 142). If m = mass of sugar in 1 c.c., α = observed angle of rotation, and l = length of tube in dms., then $m = \frac{\alpha}{l} \times a_p$. If there are other optically active substances besides sugar present, the polarisation angle, after inversion with HCl, is also taken, and the alteration in the angle of rotation gives a clue to their amount and nature. In technical analysis the scale is not graduated in arc degrees, but so as to indicate per cent. sucrose direct, when the normal weight, dissolved in 100 c.c., is observed in a 20 cm. tube. The German normal weight of sucrose is 26.048 g., and the graduations are degrees Ventzke; the French instrument reads degrees Laurent for a normal weight of 16.33 g.

1° Ventzke = 1.5931, Laurent = 0.3440 arc. 1° Laurent = 0.6277, Ventzke = 0.2167 arc.

If clarification is necessary, *e.g.*, in beet valuation, the readings must be corrected for dilution consequent on the addition of basic lead acetate, or if 10 c.c. of this solution is added to 100 c.c. of extract the sugar may be read direct in a 22 cm. tube. For details regarding the estimation and testing of sugar the reader is referred to standard treatises mentioned at the beginning of the article, or to Allen's "Commercial Analysis," vol. i. (1909), p. 289 *et seq.*

SACCHARINE AND OTHER ARTIFICIAL SWEETENING CHEMICALS

By G. Martin, Ph.D., M.Sc.

Within the last few decades chemicals of enormous sweetening power have been placed on the market. The most important of these is the **Saccharine** of Fahlberg, *o*-anhydrosulphamine-benzoic acid or benzoic sulphimide, $C_6H_4\langle^{CO}_{SO_2}\rangle NH$; discovered in 1879 by Ira Remsen and C. Fahlberg, and now manufactured by Fahlberg, List, & Co., in Salbke-Westerhüsen near Magdeburg. **Toluene** is converted into *o*- and *p*-toluene-sulphonic acid, $C_6H_4(CH_3)(SO_3H)$, by treating with concentrated H_2SO_4 at 100° C. The acid is converted first into the calcium salt (by $CaCO_3$) and then into the sodium salt (by Na_2CO_3), which is dried, treated with PCl_5 and Cl gas, whereby toluene sulpho-chloride, $C_6H_4(CH_3).SO_2Cl$, is produced. This, by treating with NH_3 gas or with Am_2CO_3, yields *o*-toluol-sulphamide, $C_6H_4(CH_3).SO_2NH_2$, which is oxidised by an alkaline solution of $KMnO_4$ to $C_6H_4.(COOK).SO_2NH_2$, which when treated with HCl is immediately converted into free *o*-sulphaminebenzoic acid, $C_6H_4(COOH)SO_2NH_2$, which then spontaneously splits off water, forming the anhydride, $C_6H_4\langle^{CO}_{SO_2}\rangle NH$, which separates out.

Saccharine is a white crystalline powder with difficulty soluble in water, melts at 223.5° C. and is *five hundred times sweeter* than cane sugar. **Easily soluble saccharine** consists of the sodium salt, $C_6H_4\langle^{CO}_{NH}\rangle N.Na$, prepared by treating saccharine with alkali carbonates.

Dulcin or **Sucrol** is another sweet chemical, about two hundred times sweeter than cane sugar. It is mono-*p*-phenetol-carbamide, $NH_2.CO.NHC_6H_4.OC_2H_5$, prepared by evaporating a solution of *p*-amidophenetol cyanate thus:—

$$C_2H_5O.C_6H_4.NH_2—(HO—C : N) \longrightarrow C_2H_5O.C_6H_4.NH—CO—NH_2.$$

It may also be obtained by heating urea with phenetidine hydrochloride,

$$C_6H_4\langle^{OC_2H_5}_{NH_2.HCl} + CO\langle^{NH_2}_{NH_2} = CO\langle^{NH_2}_{NH.C_6H_4.OC_2H_5} + NH_4Cl.$$

White needles, M.P. 173° C.; soluble in 800 parts of cold or 55 parts of boiling water, also in 25 parts of alcohol.

Other very sweet chemicals are **Glucine** (amidotri-azinesulphonic acid or its Na salt), **Sandoce** or **Methyl Saccharine**, $C_6H_3(CH_3).\langle^{CO}_{SO_2}\rangle NH$, etc.

Saccharine and similar sweetening chemicals possess no food value at all, while sugar, on the other hand, is a valuable food. The use of saccharine has on this account been made illegal in many countries as a sweetening agent for cakes, liquors, etc., intended for human consumption (except in the case of certain medicines). Saccharine must be made under Government supervision, and it is sold by apothecaries to diabetic patients as a substitute for sugar. It has considerable antiseptic or preserving qualities.

Statistics.—Saccharine is subjected to a duty of 7d. the oz. in Great Britain, the duty raised from this source being £36,000 in 1913 on 1,234,000 oz. The quantity imported in 1913 was 1,242,000 oz., of value £14,435. The quantity exported was 21,278 oz., of value £4,402. No saccharine was manufactured in the United Kingdom prior to 1903.

The United States imported 2,977 lbs. (value, $3,395) in 1908, and 1,405 lbs. (value, $1,901) in 1909; the United States export reached 2,513 lbs. (value, $2,225) in 1910; the United States duty is $1.50 per lb. and 10 per cent.

SECTION III

The Starch Industry

THE STARCH INDUSTRY

By G. Martin, Ph.D., M.Sc.

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Starch, $(C_6H_{10}O_5)_n$, is a white, glistening, tasteless carbohydrate, found in the form of small granules in the cells of grain, legumes, and potatoes. It is, next to cellulose, the most abundant material found in the vegetable world, existing in all plants with the exception of the fungi.

Starch is a condensation product of low grade sugars (hexoses), and is originally formed in the cells of the leaves of plants from the CO_2 of the air, by the aid of chlorophyll in the presence of sunlight. The starch is a migratory reserve food material, being transformed by enzymes into soluble sugars, which pass into the sap of the plant, and so it is carried throughout the plant, building it up and appearing at different stages of plant growth as cellulose, gum, lignin, etc. The microscopic starch granules have a concentrically stratified structure, similar to that of an onion. According to older ideas (Nägeli), the granules are surrounded by a sheath of cellulose, and growth occurs in concentric new layers from the kernel outwards. According to modern ideas (A. Meyer, "Untersuchungen über die Stärke," Jena, 1895), the starch granules are sphero-crystals, which grow from the centre outwards in the usual manner in the form of a cone-shaped agglomerate of fine crystalline needles, which branch off like trees, and thus extend their growth. The formation of concentric layers is due to the varying density and moisture-content of the different zones.

As regards the chemical nature of starch, Brown and Morris (see pp. 264, 265, *Beer*) consider it to have the formula $5(C_{12}H_{20}O_{10})_2$. According to Maquenne and Roux (*A. ch.*, [8], 9 (1906), 179-220), **Natural Starch** consists of two distinct substances, **Amylose** (80-85 per cent.) and **Amylopectin** (20-15 per cent.), the first being identical with Nägeli's and Brown and Heron's starch cellulose. **Amylopectin** is identical with Nägeli's "starch granulose."

Kinds of Starch.—Starch is generally obtained in Europe from potatoes, rice, wheat, and maize. In the tropics it is obtained from the palm, and tubers of various plants, *e.g.*, **sago starch** is obtained from the pith of the sago-palm (*Sagus lævis*, etc.), **arrowroot** is the starch of the *Maranta arundinacea* and *indica* (West Indies, Brazil, etc.). **Tapioca** comes from the *Manihot utilissima*, Pohl. Every species

of starch exhibits its own particular form and structural markings, so that adulteration can be detected and measured (*e.g.*, the admixture of cheap potato starch with expensive wheaten or rice starch) by microscopical examination. Each starch cell has a dark point, central in some, eccentric in others, known as the *hilum*. Round this are a series of concentric lines which give each kind of starch grain a characteristic appearance. (See Fig. 67, p. 178.)

Potato Starch has the largest granules (0.05-0.09 mm. diameter), of a characteristic mussel-like appearance.

Wheaten Starch consists of round lens-shaped cells of 0.020-0.030 mm. diameter, with a central dark point and faint markings. Mixed with these are still smaller cells, 0.002-0.008 mm. **Maize Starch** consists of characteristic polyhedronal cells, 0.015-0.020 mm. diameter, with a dark centre and no visible layers.

Rice Starch consists of very small sharp-cornered almost crystalline-looking granules, of diameter 0.003-0.007 mm., which agglomerate together to larger granules. **Tapioca, arrowroot,** and other forms of starch have all their characteristic appearances, easily recognised by experts as the result of microscopical and optical investigation (see Fig. 67, p. 178).

Potatoes yield the cheapest starch, and starch is largely manufactured from them in Germany, where over one hundred potato starch manufacturers exist, usually small in size on account of the cost of transport of the potatoes. They occur in country districts, and work only in the winter months, using the waste products, fibres, etc., for feeding cattle. Some of the larger potato starch factories produce over 20 tons of starch daily. A large proportion is converted directly into dextrine, brewing syrups, glucose, etc. Starch is also largely manufactured from rice. The largest starch rice factory in the world is Hoffmann & Co., in Salzuflen, Germany, which works over 5 tons of rice daily.

Germany is the largest starch manufacturing country. She now produces about 180,000 tons of potato starch (value about £1,300,000), 20,000 tons rice starch (value £500,000), 16,000 tons of wheat starch (value £260,000), and 9,000 tons of maize starch (£125,000). Germany also produces from starch about 56,000 tons starch syrup, 30,000 tons dextrine and starch gum, 9,000 tons glucose, and about 5,000 tons of caramel or burnt sugar, having a combined value of about £1,000,000.

Next to Germany as a starch producing country comes the *United States*, with 124 starch factories yielding 140,000 tons of starch. The bulk comes from maize (76-77 per cent.), only 14 per cent. being obtained from potatoes and 9 per cent. from wheat.

The sugary products obtained from starch are used as brewing syrups and in preparing jams, etc. (see **Glucose**). Wheat starch, being difficult to work, is not manufactured very largely now.

The following statistics show the import and export of starch into the United Kingdom :—

IMPORT.

	1909.	1910.	Value, 1910.
	Cwt.	Cwt.	
Rice starch	223,534	246,348	£241,201
Other kinds of starch	414,945	615,024	324,383
Farina and potato flour	773,993	739,615	437,286
EXPORT.			
Rice starch	58,807	64,102	£69,059
Other kinds of starch	12,258	10,062	8,296
Farina and potato flour	9,273	9,365	7,650

The United States import and export of starch is shown by the following figures :—

IMPORT.

1906.	1909.	1910.	Value, 1910.
5,422,000 lbs.	17,301,000 lbs.	10,861,000 lbs.	$296,000

EXPORT.

66,575,000 lbs.	33,228,000 lbs.	51,536,000 lbs.	$1,275,000

Properties.—Starch is a very inert body, insoluble in cold water, alcohol, ether, and cuprammonium (the latter differentiating it from cellulose). It dissolves in KOH solution, forming a potassium derivative. Starch is very hygroscopic, retaining when air-dried from 16-28 per cent. of water, and when dried in a vacuum it retains about 10 per cent. Absolutely dry starch attracts moisture with great avidity, becoming warm when moistened. When dry, starch may be heated without change to 149° C. (300° F.), but between 149° and 204° C. (300°-400° F.) it is transformed into **dextrine or British gum** (which see), a substance soluble in cold water. At higher temperatures the starch is decomposed.

Although insoluble in cold water, starch granules, when heated with water, swell up and form a paste, and in the presence of much water produce colloidal solutions. The temperature at which this "gelatinisation" occurs differs with the various kinds of starch, *e.g.*, potato starch gelatinises with water at 65° C., maize starch at 75° C., barley, kilned malt, rice, rye, and wheat starch at 80° C., while green malt and oat starch gelatinise at 85° C. The paste from wheaten and maize starch has a far greater "sticking power" than that from potato starch. The sticking power is increased by slowly drying the starch at a low temperature, and reduced by the presence of acids or alkalies and by prolonged boiling.

In general, when starch is heated alone or under pressure with water, the starch molecule breaks down into "dextrines," which are permanently soluble in cold water. This is a consequence of progressive "hydrolysis," water being gradually combined as the breakdown of the starch molecule proceeds. This conversion proceeds especially rapidly under the influence of dilute acids or diastase, the dextrines having the composition $(C_6H_{10}O_5)_m.H_2O$. The first product of the transformation is "erythro-dextrines," and which give a red or brownish colour with iodine; as the hydrolysis proceeds, the iodine coloration vanishes, achro-dextrines being produced; the final product of the action of diastase on starch is **maltose**, $C_{12}H_{22}O_{11}$. Acids hydrolyse the maltose further into two molecules of **glucose** or **dextrose**, $C_6H_{12}O_6$. This reaction is used for manufacturing glucose or dextrose from starch (see **Glucose**, p. 166).

Manufacture of Starch

It will be noticed that cereals of various sorts contain far less water than potatoes. Maize and oats are richest in fat. Regarded as a diet the cereals contain a large excess of carbohydrate and a deficiency of protein and fat. Bread and cooked cereals, however, are eaten, not as a source of protein, but as a source of **carbohydrate**, and as a diluent to the concentrated protein and fat foods. Of the cereals **wheat** and **rye** alone are suitable for making bread, on account of containing a peculiar protein, "glutin," which becomes viscid when mixed with water, and causes the binding properties of the dough.

The following table shows the percentage of starch in the chief raw products used in its manufacture :—

	Rice (husked).	Wheat.	Maize.	Potatoes.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Starch (inclusive of sugar and dextrine)	76-80	70.0	68.5	20.0
Cellulose fibre, pentosane, etc.	0.6	2.5	2.5	0.8
Nitrogenous substances	7.8	12.4	9.9	2.0
Fats	0.5	1.7	4.6	0.2
Ash	1.4	1.8	1.5	1.0
Percentage of dry substance	86-90	88.4	87.0	24.0

Rice Starch.—Rice, *Oryza sativa*, contains a higher percentage of starch (76-80 per cent.) than any other grain, but, on account of the extreme minuteness of its starch granules, and the presence of gums and albumens which firmly cement the cells together, is one of the most difficult substances to work for pure starch. For this reason the operation is usually undertaken only by very large industrial manufactories, and bruised rice is usually employed.

The process is as follows:—The rice is soaked with a very dilute solution of NaOH (0.3-0.6 per cent. solution, a stronger solution gelatinises the starch) in large cemented tanks. This dissolves the gums and nitrogenous matter cementing the starch cells together. The wet rice is then finely ground between millstones, keeping it moist during the process with NaOH solution. The grinding finally disintegrates the agglomerate of starch cells into the individual cells. The mass is next transferred to vats provided with stirring apparatus, and a milky suspension of the fine starch particles is obtained, the cellulose, fibres, and heavier constituents sinking to the bottom. The starch milk will not easily and quickly deposit the starch by sedimentation (as is the case with potato starch), on account of the extreme smallness of the rice-starch granules. Consequently to extract the starch, the milky liquid is transferred to rapidly rotating centrifugals, the drums of which are *not* perforated to allow the water to escape. As the result of the centrifugal force, the starch granules settle out as a compact ring on the interior circumference of the rotating drum, the outermost layers being practically pure starch, while the internal part of the ring is composed of impure starch, mixed with cell fragments of mixed starches. In the middle of the drum the water settles out as a clear liquid; this is run off, and the compact ring of starch is taken out, and the interior impure layer scraped off and made to undergo the same process again. It is usually necessary to add a trace of ultramarine to the starch in order to obtain a pure white. The starch is then cut into 7-in. cubes, pressed in iron forms until the water content is diminished to 45 per cent., and then slowly dried in drying chambers. When the amount of water reaches 29 per cent. the surface layer of starch is scraped off. This layer is of a yellowish colour and contains a considerable quantity of impurities which have diffused out with the water from the interior of the cake to the exterior, and been left behind by the evaporating water. The residual cake of starch is now packed in cardboard or paper boxes, and dried until peculiar longitudinal fissures or cracks appear. It has then 12 per cent. of water.

During the process of drying great care must be taken to guard against the development of *moulds* on the surface of the starch—a result of the incomplete separation of the nitrogenous matter—such moulds often completely spoiling the goods.

The alkaline liquid or "lye" separated from the starch during the grinding and soaking process contains a considerable amount of nitrogenous matter in solution. The dissolved matter is precipitated by H_2SO_4 as a glutinous mass, which, when dried, forms a valuable cattle food. The other waste liquids from the manufacture are valuable manuring waters for meadow lands, and are used as such. Their escape into small streams is dangerous.

Rice starch has great sticking power, and is nearly twice as valuable as potato starch (*q.v.*). On account of the smallness of its grains it may be used in a powdered form for stiffening linen in laundry work.

Wheat Starch.—A grain of wheat consists of (1) the germ, (2) the endosperm or kernel, (3) the outer envelope or husk, which constitutes the bran. The husk has an outer cuticle from which delicate hairs spring, under which are three other layers, the two outer of which consist of flattened cells. Then comes the envelope of the seed, the "testa" or "episperm," which encloses the endosperm (see Fig. 68).

The envelope of the seed consists of angular cells filled with a mixture of soluble and insoluble proteins, which with water form a thick viscid mass, and when dried has a horny appearance. This is the "gluten," and its presence determines the binding quality of dough made from wheaten flour or rye. The **gluten** does not exist as such in the grain or flour, but is developed by the interaction in the presence of water of two proteins, **gliadin** and **glutenin**.

Barley Starch. × 240.

Tous-les-mois Starch. × 240.

Potato Starch. × 240.

Rice Starch. × 240.

Wheat Starch. × 240.

Rye Starch. × 240.

Maize Starch. × 240.

Arrowroot or Maranta Starch. × 240.

Oat Starch. × 240.

Tapioca. × 240.

Tapioca Starch. × 240.

Curcuma Starch. × 240.

Sago Starch. × 240.

Sago. × 240.

FIG. 67.—TAKEN FROM GREENISH'S MICROSCOPICAL EXAMINATION OF FOODS AND DRUGS.
By kind permission of Messrs J. & A. Churchill.

[To face page 178.

The **endosperm** consists of (A, Fig. 68) large starch cells provided with delicate walls, and filled with starch granules.

The husk ("bran") consists principally of cellulose with pigments and mineral matter. The endosperm is mainly starch. The germ (B, Fig. 68)—forming only a small proportion of the whole—is rich in protein and fat. For **chemical composition** of wheat, see p. 178.

For the preparation of flour the grain is ground or milled in iron roller mills and the various constituents of the grain separated. The outer coats yield **bran, fine pollards, sharps, and middlings**; the **endosperm** yields ordinary wheaten flour; the germ is removed as "offal."

The flour is sorted out by machinery into—.

(1) A smaller portion of very white flour known as "patents." It is very poor in proteins and is the flour from which genuine Vienna bread and the best fancy breads and pastries are made.

(2) A larger portion known as "bakers' flour."

The **semolina**, which is obtained from the central part of hard wheat and which is rich in gluten, is also removed from white flour.

Hence ordinary white flour (and white bread made from it) contains no bran, germ, or semolina, and consequently valuable food constituents (mineral matter and protein from the semolina and bran, protein and fat from the germ) are absent from it.

Wholemeal flour (and wholemeal bread) includes these constituents, and is consequently much richer in nitrogenous and mineral foods than white bread. Wholemeal bread, however, irritates delicate stomachs on account of the cellulose and silica of the outer coat.

Recently the outer layers of the husk have been removed, and with it the irritant material, and a flour has been put on the market containing the valuable mineral, protein, and fatty constituents of the inner branny coat, germ, and semolina. This is the so-called "80 per cent. flour" and is used in making "Standard bread." By "80 per cent. flour" is meant that from 100 lbs. normal wheat (*i.e.*, 1 bushel weighing 64 lbs.) 80 lbs. of flour are obtained.

The food known as **Grape-Nuts** is derived solely from **cereals**, the constituents of which are rendered more digestible than in the raw cereal (probably by a process of malting followed by roasting). This is evident from the remarkable solubility of the preparation, nearly 50 per cent. of which is soluble in cold water. The soluble portion contains no starch, being chiefly dextrine. The following gives an analysis of a sample of "Grape-Nuts": moisture, 6 per cent.; mineral matter, 2 per cent.; fat, 1.6 per cent.; proteids, 15 per cent.; soluble carbohydrates, etc., 49.4 per cent.; unaltered insoluble carbohydrate, 26 per cent.; the mineral matter is rich in phosphoric acid. It is placed on the market by the Postum Cereal Co. Ltd., Battlecreek, Michigan.

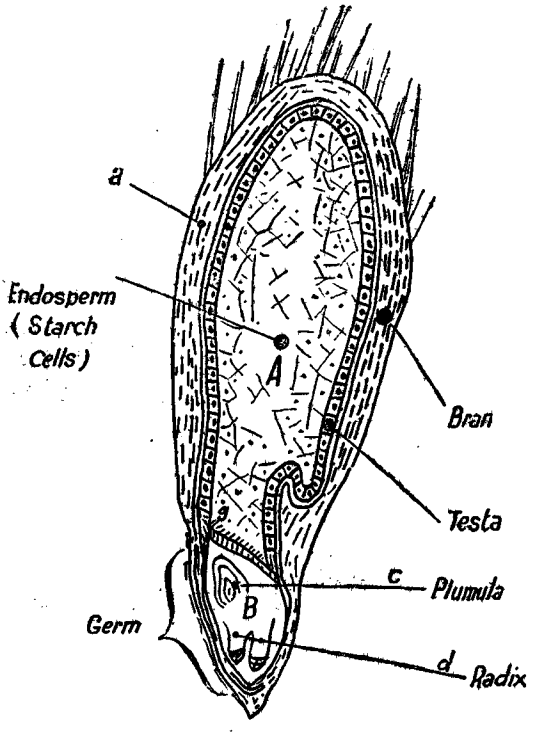

FIG. 68.—Wheat Grain.

The process now usually adopted for working wheaten flour for pure starch is the *Sweet Process*. The flour is mixed with a small amount of water to a stiff dough, placed in special kneading machines, and the excess of water kneaded out. Most of the starch goes into suspension in the water, forming a milk, while the sticky gluten and cellulose fibres remain behind as a thick soft mass. The open kneading machine most used for the process is seen in the illustration. It consists of a trough in which two kneading arms are worked in opposite directions, one directly by means of a pulley and the other indirectly by means of toothed wheels. The wings revolve at different rates, so that no clogging can occur. The starch milk is

emptied out of the trough from time to time, the last traces being removed from the remaining gluten by passing the mass through rollers.

The starch milk is separated into pure "Prima" starch and glutinous "secondary starch" by centrifugalling in special drums, which are non-perforated, the process being exactly the same as described in the manufacture of rice starch. The drying is also carried out as with rice starch, similar fissures making their appearance in the dried mass as is the case with rice starch, the fissured appearance differentiating the valuable wheaten and rice starch from the cheaper potato starch. Even on adding glutinous material to potato starch it is impossible to obtain this fissured appearance.

The gluten-rich secondary starch is either directly used as food (also as cattle food) or is allowed to spontaneously ferment at 50° C. (see below) when a further yield of starch is obtainable.

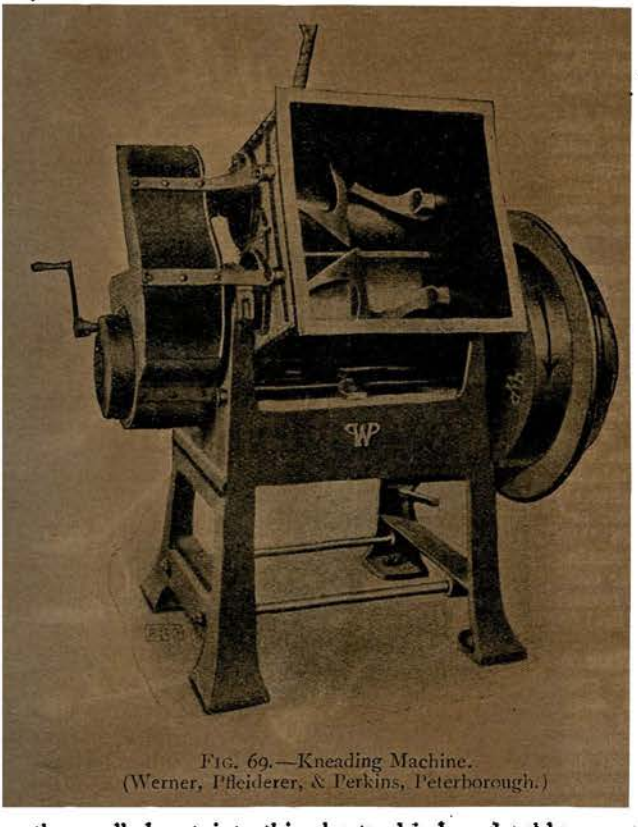

FIG. 69.—Kneading Machine.
(Werner, Pfleiderer, & Perkins, Peterborough.)

In Germany wheaten starch factories are often run directly in connection with a bakery. The flour is kneaded out with water and the starch milk is separated as above described and worked for pure starch by means of centrifugals. In this way, 60-75 per cent. of pure starch is obtained. The glutinous residues are then used for baking.

With proper care 100 parts of flour yield 60 parts pure "prima starch," 10 parts "secondary starch," and 10 parts of the sticky gluten. The gluten is difficult to completely dry, and being a proteid, in a wet condition rapidly undergoes putrefaction. In a dried and powdered condition attempts have been made to place it on the market under various trade names, *e.g.*, "Albumen Powder," "Aleuronate," etc., but with little success. Usually it is allowed to putrefy at about 50° C. for some time, when it acquires gummy properties, and is then rolled out into thin sheets, dried, and sold as a paste called "**Shoemakers' Paste.**" No other paste adheres so well to leather as this paste, and with it leather can be secured not only to leather but also to woven materials, paper, etc.

Formerly, and to some extent at the present time, crushed wheat was worked for starch by moistening with water and allowing fermentation to set in, lactic acid being formed and the gluten largely dissolved. The starch granules could then be easily washed free from the gluten. The residues could only be used as cattle food.

Potato Starch.—The potato contains from 16-22 per cent. of starch, 1.5 per cent. of sugar and dextrine, and 76 per cent. of water. (See p. 178, Table.)

In Germany very large amounts of starch are obtained from potatoes; 3 per cent. of the total potato production going for the manufacture of starch, 6 per cent. being utilised for industrial alcohol and spirits, the rest being consumed as food.

In Germany the potatoes are usually worked for starch in small factories situated in country districts, which usually work only in the winter months and employ the waste from the manufacture directly as cattle food.

The potatoes, when kept, lose considerably in weight through internal breathing and loss of water by evaporation. Consequently, in order to diminish loss, they are stored after harvesting in dark, cool cellars. If allowed to freeze they become sweet owing to the accumulation of sugar in consequence of the cessation of breathing (which consumes the sugar, evolving it as CO_2). When germinating in spring a large amount of starch is lost (see under **Malt**), being used as food for the growing plant. The germ contains the poisonous alkaloid **Solanin**. Potatoes are invariably worked for starch during the winter months.

The percentage of starch in the potatoes is usually estimated by taking their specific gravity by means of Reimann's potato balance, the potatoes being weighed in air and in water. If Wa = weight in air, and Ww = weight in water, then their specific gravity S is given by $S = \frac{Wa}{(Wa - Ww)}$.

Direct experiments have shown that there is a connection between the specific gravity and the starch contents. The following figures are taken from *Behrend & Morgen's* Table:—

Specific Gravity of Potato.	Starch.	Specific Gravity of Potato.	Starch.
	Per Cent.		Per Cent.
1.080	13.9	1.120	22.5
1.090	16.0	1.140	26.7
1.100	18.2	1.159	30.6
1.110	20.3		

Young or diseased potatoes are unsuitable for starch manufacture, the former containing small undeveloped starch granules, and the latter having the granules partially destroyed, which renders the isolation of pure starch difficult.

The larger the starch granules in a potato the better the yield and quality of the prima starch.

Attempts have been made in Germany to increase the starch content of potatoes by selective cultivation, much in the same way that the enrichment in sugar of the sugar-beet has been effected (see **Sugar**, p. 144), but up to the present, however, with little success.

Manufacture.—The potatoes are first washed in special machines, and then cut up into a fine pasty mash by special cutting machines. The starch is washed out of the pasty mash by water. The residual fibrous matter, consisting principally of cellulose, is used for feeding cattle, and sometimes for making glucose. A brush extracting machine is used for washing out and removing the starch granules from the potato mash, the starch being obtained as a milky suspension in water. The brushes are arranged spirally round the axis of the machine, and cause the potato pulp to traverse it from end to end, subjected meanwhile to the washing effect of water. The cellulose fibres are separated by sieves, and the milky starch suspension is run either through troughs inclined at a very small angle, or into large cemented tanks. The starch sinks to the bottom and is collected, washed again in tanks with pure water, allowed to settle, and the upper layer of starch, which is impure and greyish in colour, is scraped off. By repetition a perfectly pure moist starch is obtained, containing 50 per cent. of water. The starch is now dried. In the process it must not at first be heated beyond 40° C., or it begins to swell up and gelatinise. The introduction of centrifugal machines for drying has been attended with beneficial results, the centrifugal drums being provided with fine cloth, which allows the water to pass through, but not the starch. The starch is centrifuged until it contains 30-35 per cent. of water. It is then transferred to special basketwork frames or drying apparatus, and dried in warm air at 30° C. until it contains 17-20 per cent. of water. It is not dried beyond this, because if this were done the dried

starch on exposure to ordinary air would again rapidly absorb moisture until this percentage is attained. Potato starch is the cheapest kind of starch, being only half the price of the best rice or wheat starch.

From 80-90 per cent. of the starch in the potato can be isolated by careful work, and it comes into the market in a ground condition as a fine white powder called "Potato Flour."

Two qualities are usually sold, namely, **Prima Potato Flour**, snow white, with only a trace of nitrogen, fat, and ash (less than 0.5 per cent.), and **Secondary Potato Flour**, which is grey in colour, and contains a certain amount of nitrogenous bodies, fats, etc.

Potato starch is sometimes put on the market in a *granular form* ("**Artificial Sago**"), by mixing the damp starch with a little dextrine solution, rubbing the mass through sieves with 3-5 mm. mesh, rounding the particles in a rotating drum about 15 ft. long, dusting with powdered starch, sieving and drying at 100° C. in a chamber until a glaze is formed, then drying at a lower temperature. It is often sold as "sago" and has the same nutritive value as true sago.

The pulp left behind after the extraction of the starch amounts to about 20 per cent. of the original weight of the potato, and contains 10-20 per cent. of the total amount of starch originally in the potato, as well as much cellulose fibre, nitrogenous matter, and ash. It is either dried to 70 per cent. water and used as provender for cattle, in a fresh condition, or dried further, mixed with oil cakes, compressed, and sold in the form of cakes for cattle. The juice and liquor from the potatoes is rich in nitrogen, potassium, and phosphorus, and is used for manuring land. Potatoes contain 0.25 per cent. N, 0.2 per cent. P_2O_5, and 0.6 per cent. K_2O. (See Table, p. 178.)

Maize Starch or Corn Starch Manufacture, now an enormous industry in the United States, is carried out by steeping maize in large hopper-bottomed wooden vats with water containing 0.3-1 per cent. of sulphur dioxide, SO_2. The steeping lasts two to four days, the hot SO_2 water being kept in circulation by steam siphons and heat is supplied to maintain the temperature at 40°-50° C. (120°-140° F.).

The steep water is either run to waste or evaporated to recover the soluble extract as cattle food.

The disintegrated grain is crushed in a Foos mill and stirred up with water. There remains a sediment of unground maize (which is reground) while the finely ground portions pass away suspended in water through a large V-shaped tank (the "Degerminator") fitted with a screw conveyer in the bottom and skimming paddles at the top. The **germ** of the maize floats and is skimmed off by the paddles and so separated.

The separated germ is washed free from starch, cooked with live steam, and "**maize-oil**" or "**corn-oil**" is manufactured by pressing, the solid residue being sold as a cattle food, as "**oil-cake**" or "**maize-germ cake.**" See p. 44.

The endosperm, starchy and dextrinous matter, bran, fibres, etc., pass on in the liquors, known as **separator-liquors.** These liquors are first of all passed over vibrating copper sieves, which retain the coarser particles, bran, fibre, etc., the starch suspension passing on to other sieves.

The coarse material retained by the copper sieve at this stage is caught in elevators, conveyed afresh to the grinding mills, ground with water in burr-stone mills, pumped to mechanically stirred feed vats, and the liquor coming from these is united with the above mentioned "separator liquors" coming from the degerminator.

The starch-containing liquors coming from the copper sieve now pass over a series of sieves known as "shakers," being made of No. 10 bolting cloth stretched over wooden frames. These receive a vibratory motion from an eccentric shaft, the shakers being set on hickory sprains to give a rapid but soft motion. The starch cells pass through as a milky liquor, while a mass of grain and bran is left behind on the sieves ("shakers").

This residue is stirred with water to wash out starch, then pressed and sold as "**press feed**"; or it is dried and sold as "**corn bran.**" It contains: Proteids, 10.5 per cent.; fat, 2.75; carbohydrates, 65.0.

The milky liquor running through the sieves is known as "mill liquor" or "crude starch liquor." It contains the starch as a fine suspension, 1 gal. containing

5.4 oz. pure starch and 1 5 oz. of "dry feed." Its specific gravity is 3° Bé. It is (sometimes) run through another series of sieves (to remove fibres, etc.) and then is made to flow over a long series of wooden gutters (usually made in sixteen sections, each 120 ft. long and 6-7 in. deep, and each section divided by wooden partitions into three channels each 18 in. wide and having a slope of $\frac{3}{8}$ in. in every 12 ft.). The speed is 1 gal. per thirty-five secs., the entering density of the liquor being 3.5° Bé. The starch granules are here almost completely deposited, the outflowing liquid only possessing the specific gravity of 0.5 Bé. and escaping at the rate of 1 gal. per twenty secs.

The escaping liquors are either run into settling tanks, settled, and the supernatant clear liquid siphoned off and the fluid mass underneath sold as a cattle food ("**swill**" or "**slop**").
Sometimes the sediment is pressed and sold as "**gluten-meal.**"

The starch which has deposited in the gutters or runs is now shovelled out. It contains 50 per cent. water and is impure. It is made into a paste of 7° Bé. with water in large wooden vats ("breakers") provided with stirring gear, and a solution of caustic soda of 3° Bé. run in until the liquid turns greenish yellow. The alkali neutralises acidity, precipitates some proteid, emulsifies or dissolves any oil.

The fluid is now diluted to 3.5° Bé. in vats, and once more sent down the separating gutters. The starch separated this second time is once more mixed with water, run into shallow pine-wood draining boxes, provided with perforated bottoms. The moisture drains off overnight and the blocks of moist starch (55 per cent. H_2O) are then dumped out of the boxes on to the drying floors.

Very often the starch after coming from the gutters after the alkali treatment is further purified by mixing with water to 11°-12° Bé., and is then placed on a series of sieves or shakes, where any coagulated material separates, the starchy fluid pouring through at 8° Bé. This liquid is then settled, the supernatant liquid run off, fresh water added, and the mass, of sp. gr. 24° Bé., is run into the draining boxes as above described. Sometimes the alkali treatment is omitted, this "unchemicalled starch" being used for baking powder, or as size in the textile industries.

The drying of the starch is best done in vacuum. The purified starch paste is first run into boxes lined with linen, and placed in a vacuum chamber. Rapid drying takes place in a few hours. The starch in these boxes is cut into 7-in. cubes, placed in a hot air drying chamber provided with an exit for moist air. In the stream of dry air the starch completely dries in a few hours.

In the old system of drying (still used), the starch was first dumped on to drying floors made of porous brick, covered with plaster of paris, and heated by steam pipes from beneath. Here the moisture content is reduced from 55 per cent. to 45 per cent. The starch is now crushed, placed in small blocks on shelves in a hot air drying kiln, and dried at 120°-130° F.
The yellowish crust which forms on the outside is scraped off, and the blocks redried at 156°-176° F. for three to sixteen days. The scrapings are worked for starch, using alkali as before.
Maize yields 59 per cent. of starch, decorticated maize giving 68 per cent.

Maize starch is put on the market as (1) **Thin boiling starch** prepared by suspending **unchemicalled starch** in water (22° Bé.), adding hydrochloric acid to the water in the mills, then boxing and draining and drying the starch as described above. The HCl converts some of the starch to a soluble form, whereby it yields a paste of low viscosity. This is the "drying-in" process. In another process, called the "in-suspension" process, the suspension of starch in water (22° Bé.) is heated to a temperature well below the gelatinisation temperature with a little HCl or H_2SO_4, with continual stirring. The starch is then run into boxes and dried.

The thin boiling starches are used in laundry and confectionery work, and produce a thin paste.

(2) **Thick boiling starch** is the ordinary starch, dried slowly as above described. When very thick boiling starches are wanted, either for use in baking powder or as size in the textile industries, the treatment with alkali (see above) is omitted, the starch being merely run through the gutters or runs a second time and dried slowly. The protein is thus not removed, and so the material has a greater "agglutinating" power.

The starches "**Mondamin**" and "**Maizena**" are prepared from maize.

Cornflour is made from maize or Indian corn, large factories existing at Paisley in Scotland, the process of manufacture being very similar to that above described. Rice starch, similarly treated, is sold for dietetic purposes as "British Cornflour," etc.

Manufacture of Arrowroot. — The roots of the plant *Maranta arundinacea* are collected, thoroughly washed, and the skin removed with suitable knives. The skin, if left on, discolours the starch and imparts to it an unpleasant flavour (owing to resins contained therein). After removal of the skin the roots are washed, pulped by crushing between copper rollers, or by pressing against water, and the pulp is transferred to upper cylinders provided with small perforators, where it is thoroughly agitated and treated with a current of water.

The starch is thus separated from fibre, etc., and is carried away in the milky liquid issuing from the cylinders, the woody matter, etc., remaining behind. The liquid is now filtered through fine muslin sieves (to separate any floating fibre) and is then allowed to settle in reservoirs, when it is washed with fresh portions of clean water after each settling. The starch is then transferred to shallow copper pans, covered with fine white gauze (to protect from dust, etc.), and allowed to dry. When dry it is packed in small barrels for shipment.

The composition of the **roots** is given by Leuscher (*Journ. Chem. Soc.*, 1902), as: H_2O = 63.4 per cent.; starch = 27.8 per cent.; dextrin and sugar = 2.08 per cent.; fibre = 3.9 per cent.; ether extract = 0.19 per cent.; proteid = 1.64 per cent.; ash = 0.89 per cent. **Arrowroot starch** contains: starch, 83.7 per cent.; H_2O, 15.9 per cent.; fibre, 0.04 per cent.; sugar, gum, 0.18 per cent.; ash, 0.14 per cent.; proteid, 0.0.

Tapioca is prepared from the *Cassava* or *Mandioc* plant of South America. The tubers are washed, peeled, pounded to pulp, pressed in baskets to expel the poisonous juice, and the meal thus obtained is sifted (to remove fibre), dried by gentle heat (never sufficient to colour the meal), which expels the last traces of the poisonous juice. **Cassava starch** is prepared by repeatedly washing the fine meal with water, the sediment allowed to settle, the water decanted, and the starch is sun-dried. **Tapioca** is made from the moist starch by heating on metal plates. The starch grains swell, burst, and become agglutinated into the commercial granular "tapioca."

Manufacture of other Varieties of Starch.—Starch is also manufactured from various other tropical plants, *e.g.*, Curcuma, Tacca, and Sago. Sago starch is obtained by kneading with water the pithy interior of the sago-palm. "**Pearl sago**" is obtained by forcing the moist sago starch through sieves, rolling in cloth, and heating with a little fat in pans. Pearl sago contains: starch, 84.6 per cent.; H_2O, 15.2 per cent.; ash, 0.11 per cent. Large amounts come from Singapore. A similar granular substance made from starch meal is known as "**Artificial Sago**" (see under **Potato Starch**).

Soluble Starch is obtained by boiling starch with water, the solution being rendered quite clear by the addition of a little caustic alkali. If starch paste is heated to boiling under 2-3 atmospheres pressure a strongly dextro-rotatory solution ($[\alpha]_D = +198°$) is obtained, which gives a deep blue colour with iodine; the addition of alcohol causes the precipitation of the "soluble starch" as a white powder, which, however, will not again completely dissolve in cold water.

Other ways of rendering starch soluble are: stirring starch powder with a solution of caustic soda, also by stirring with water and warming with malt (diastastic action), dil. H_2SO_4, or bleaching powder.

A recent patent (German Patent, 134,301) describes the manufacture of a soluble starch by mixing 100 kg. of starch flour with 3-5 kg. of ammonium persulphate and 150 l. of cold water, standing for ten hours, filtering and washing until free from persulphate, and drying. The nascent O from the persulphate $[(NH_4)_2S_2O_8 + H_2O = 2(NH_4).HSO_4 + O]$ acts on the starch and renders it soluble.

The product dissolves in hot water to a clear solution which solidifies on cooling to a jelly. Used in dressing textiles.

Boiling with a volatile organic acid (formic or acetic, German Patents, 182,558 and 137,330) also renders starch soluble. The acid may be easily distilled off, and neutralisation is unnecessary.

Starch is also rendered soluble by treating it with Cl gas and then heating to 100° (German Patents, 149,588 and 168,980), by treating with $KMnO_4$ (German Patent, 156,148), by heating powdered starch to 62°-63° C. with HCl vapour (American Patent, 773,469), etc., etc. **Ozone** renders starch soluble.

A starch which has the power of swelling up with cold water is made (German Patent, 157,896) by stirring between 10°-30° C. with 50-80 per cent. of methyl or ethyl alcohol, so as to make a thin milky liquid suspension of starch. To 100 parts of the mixture 40 parts of caustic soda solution (30° Bé.) are added, and then after some hours' standing, acetic acid. The starch is pressed out of the wet alcoholic solution, dried and ground. Useful for dressing textiles and for manufacturing adhesives.

A similar starch is made by stirring starch with warm Na_2SO_4 solution, adding $NaOH + Na_2SO_4$ solution, standing for ten minutes, pressing, drying and powdering (German Patent, 166,259). See also **Dextrine**.

Bleaching Starch.—The practice of bleaching flour and starch has been declared by some authorities to be a highly deleterious one, while others assert that the custom is harmless. The process is carried out by exposing the starch or flour to the vapours of **Nitrogen Peroxide**.

Uses of Starch.—Besides being used as a food, starch is used in the arts for a variety of purposes, most of these depending upon its capacity for gelatinising with water and forming a paste. Starch is used:—

1. In laundry work for stiffening linen collars, shirts, etc. The gelatinised starch is applied in a thin layer over the article, and is converted by the passage of a hot iron into a shiny stiff layer of **dextrine** (which see). The **starch glazes** are made by adding borax, finely powdered stearic acid, or paraffin to potato starch, and give a shining silvery lustre. Potato starch is the cheapest variety of starch, and so is largely used for this purpose. Wheat starch or, still better, rice starch (which can be used with cold water, thus avoiding the trouble of boiling with water necessary with potato starch) are superior to potato starch for laundry purposes, but are dearer. By mixing starch with azo-dyes coloured starches can be obtained, which wash white again.
2. As an adhesive, much is used by the paperhanger, bookbinder, etc. Potato starch forms a poor adhesive; wheat or maize starch are much superior for this purpose. "**Gloy**" is said to be a mixture of dextrine and starch with magnesium chloride (see **Dextrine**).
3. Many mixtures of starch and dextrine are employed as thickening agents for colours and mordants in calico printing, etc. etc. The pastes must be free from acid and alkali.
4. For sizing paper, a mixture of starch paste and rosin is used.
5. Thin starch pastes are largely used for finishing and weighting calicoes, lace curtains, and cloths. Such pastes must be thin, and wheat starch is the best for the purpose, since it sinks into the fabric more thoroughly than potato or maize starch. The cloth is, after soaking in the paste, passed through hot rollers, and so finished with a fine glaze.
6. Fine rice starch is used as a face powder. Fine starch is also used for dusting moulds in metal founding.
7. As a thickening agent for sauces, puddings, etc. etc.
8. Large quantities of starch are worked up into dextrine (or British gum), brewing and preserving sugars or dextrose, glucose, burnt sugar or caramel for colouring beer, etc. etc.
9. In a non-isolated condition the starch of potatoes and grain serve as a food (bread, etc.), and as the source of alcohol in beer and spirits, all of which are manufactured from starchy material.

Estimation of Starch, Testing Starch.—The amount of starch in grain and potatoes is determined by hydrolysing the starch completely into dextrose with very dilute HCl. The starch-containing material in a finely divided condition is first heated in an autoclave at 3 atmospheres with water, or diastase is added. The starch is thus dissolved in the water, the cellulose and fibres remaining behind and are separated by filtration. The clear filtered starch solution is now converted into dextrose (by heating with dil. HCl), which is estimated in the usual way with Fehling's solution. 100 parts of dextrose are obtained from 92-93 parts of starch (theory = 90).

Qualitatively the presence of starch may be detected by the blue colour it gives with iodine.

A microscopic examination (see p. 176) determines the nature of the starch (rice, potato, wheat, etc.,) and whether adulterated. Good starch should not contain more than 20 per cent. water, which is estimated by heating 10 g. starch to 40°-50° C. (not higher) for one hour, then to 120° C. for four hours, cooling in desiccator, and weighing.

Acids, if present in the starch, are estimated (Saare) by stirring 25 g. starch with 30 c.c. H_2O to form a thick paste, and titrating the paste with $\frac{N}{10}$ *NaOH* until a drop of the solution placed on a folded filter paper is not coloured red with litmus; a control experiment is necessary, using neutral starch. 100 g. of a *slightly* acid starch require 5 c.c. $\frac{N}{10}$ NaOH. The starch is *acid* if it requires 8 c.c. $\frac{N}{10}$ NaOH, and *strongly acid* if *more* than 8 c.c. are required for neutralisation.

The adhesive power of the starch is determined (Scheil) by mixing 4 g. with 50 c.c. water, and boiling over a Bunsen burner until the paste is transparent and begins to froth. The burner is removed and paste well stirred. The heating must not last for more than one minute. 4 g. in 50 c.c. of H_2O of a normal starch sets, on cooling, to a paste which cannot be poured out of the dish.

Impurities may be estimated in the ash of the starch, or in the residues left after dissolving out the starch. Starch is easily brought into solution by warming at 65° C. for two hours with a normal malt solution (100 g. malt in 1 litre water).

DEXTRINE, BRITISH GUM, STARCH GUM

When starch is heated to 180°-200° C. for a short time, or when moist starch paste is heated with a trace of acid, best with HCl or some other easily volatile acid, it is converted into a thick gum-like mass, possessing powerful adhesive properties, and which is in consequence largely used as a substitute for the expensive **gum-arabic**.

Dextrine is not such a powerful adhesive as gum-arabic, and papers covered with it easily become moist in wet weather, but it is far less expensive, and consequently is much used as the gum for paper labels, stamps, envelopes, etc. It has the advantage over starch as an adhesive that it dissolves in cold water and need not be boiled. Mixtures of dextrine and starch paste are on the market as adhesives ("Gloy" is said to be such a mixture with magnesium chloride) and as a thickening agent in colour printing.

Dextrine is prepared from starch in two ways:—

1. **The Acid Process.**—This is steadily gaining ground; it consists in taking the damp "green" starch, fresh from sedimentation, and mixing with it 0.2-0.4 per cent. of concentrated hydrochloric or nitric acid and heating in open pans in a closed chamber heated to 150° C. The acids volatilise and the dextrine is left as a yellowish glassy mass, which usually contains a small amount of starchy matter insoluble in water, and a small percentage of dextrose.

2. **The Roasting Process.**—The starch is heated without acids in rotating cylinders to a temperature of 180°-200° C., the starch being fed in at one end and removed as dextrine at the other. In Lehmann's process the starch is placed in closed vessels provided with powerful stirring apparatus and heated at the bottom by superheated steam to the necessary temperature. It yields a better product than the rotating cylinder method.

"Crystallised British gum," "crystallised gum," etc., is simply dextrine which has been decolourised with animal charcoal and evaporated down until on cooling it gives a light coloured brittle mass, similar to dried gum-arabic.

Statistics.—In 1910, about 92,000 cwt. of dextrine, of value £63,000, were imported into England, and 3,800 cwt., of value £3,200, were exported. The United States in 1910 imported 6,392,000 lbs. (value, $197,000).

Shoemakers' Paste (see p. 180) is also a dextrine. See also under **Glue, Gums.**

For the manufacture of **Starch Syrups**, starch sugar, glucose or dextrose, see under **Glucose.**

SECTION IV

The Cellulose Industry

THE CELLULOSE INDUSTRY

By A. J. Carrier, B.Sc., and G. Martin, Ph.D., M.Sc.

I.—CELLULOSE, $(C_6H_{10}O_5)_n$

LITERATURE

See also under "Paper-Making," "Celluloid," "Artificial Silk."

Article on "Cellulose" (Dr Frankland Armstrong) in Allen's "Commercial Organic Analysis," vol. i., 1909, third edition, where analytical methods are discussed.

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O. Dammer.—"Chemische Technologie der Neuzeit." Articles on "Cellulose," "Celluloid," "Artificial Silk," etc. Stuttgart, 1911.

E. C. Worden.—"Nitrocellulose Industry." 2 vols. London, 1911.

Cellulose forms the basis of the solid framework of plants, and is the most widely-distributed carbohydrate of the vegetable kingdom. It occurs nearly pure in cotton, linen, and in the pith of many plants. Cellulose forms the raw product for the manufacture of paper, nitro-cellulose (gun-cotton), celluloid, artificial silk, and similar products.

Cellulose is obtained very largely from wood, grasses, and, in small part, from straw. Among plants which are largely cultivated as sources for cellulose may be mentioned cotton, flax, hemp, jute, esparto, China grass or ramie, etc.

The formula for cellulose is $(C_6H_{10}O_5)_n$. The molecular weight is unknown, but is undoubtedly very high.

Cellulose is more stable than starch. When air-dried, it contains 6-12 per cent. of water, which is driven off at 100° C., but is re-absorbed on exposure to air. Several cellulose hydrates exist, which give an indigo-blue coloration with iodine in aqueous solution. Treated with dil. HNO_3 or chromic acid, cellulose is oxidised to an oxycellulose; concentrated HNO_3, however, nitrates it. (See **Gun-Cotton, Collodion,** etc.) Prolonged boiling with dilute acids converts cellulose into hydrocellulose, $(C_6H_{10}O_5)_n.H_2O$, which is distinguished from cellulose by containing free carbonyl groups, and the greater reactivity of its OH groups.

The acetyl compound, $C_{12}H_{14}O_4(O.CO.CH_3)_6$, an amorphous mass soluble in $CHCl_3$, is produced by heating cellulose with acetic anhydride to 180° C.

Concentrated sulphuric acid causes cellulose to swell up and dissolve to a paste-like compound called amyloid, which is precipitated by water. If the solution be greatly diluted and heated to 120° C., an almost quantitative yield of dextrose is produced. This when fermented yields alcohol—one of the suggested methods of obtaining alcohol from wood.

The enormous magnitude of the cellulose industry (including wood and timber, paper, wood fibre, celluloid, etc.), may be gauged from the following statistics:—

IMPORTED INTO THE UNITED KINGDOM.

	1906.	1910.	Value in 1910.
Wood and timber	10,080,000 loads	9,820,000 loads	£24,350,000
Furniture woods, hard woods	279,000 tons	270,000 tons	1,870,000
Manufactured wood	...	...	2,340,000
Paper	452,000 tons	548,000 tons	6,410,000
Paper-making materials	834,000 ,,	1,085,000 ,,	4,970,000
Celluloid ware	...	....	450,000
Artificial silk	...	...	40,000
Total value	...	...	£40,430,000

EXPORTED FROM THE UNITED KINGDOM.

	1906.	1910.	Value in 1910.
Wood, timber, and manufactured wood	...	...	£1,960,000
Paper	71,000 tons	144,000 tons	3,120,000
Paper-making materials	112,957 ,,	165,217 ,,	744,000
Xylonite and celluloid ware	...	...	167,000
Artificial silk	...	...	196,000
Total value	...	...	£6,187,000

The magnitude of the United States cellulose industry is shown by the following figures:—

	Import, 1910.	Export, 1910.
Wood, and manufactures of	$54,422,000	$78,814,000
,, unmanufactured	51,221,000	
Paper, and manufactures of	17,536,000	16,083,000

For *details*, see under special articles. For linen, cotton, jute, etc., see under **Textile Fibres.**

Estimation and Valuation of Cellulose.

1. The percentage of cellulose in a sample is best determined by Cross and Bevan's chlorination process (*Trans. Chem. Soc.*, 1889, 55, 199). 5 g. of the fibre dried at 100° are boiled for half an hour with 1 per cent. NaOH, washed and squeezed to remove NaOH and water, placed in a beaker and subjected to a slow stream of chlorine. The non-cellulose portions (lignin, etc.) form soluble chlorinated products. After thirty to sixty minutes' exposure the product is washed, heated to boiling with a 2 per cent. sodium sulphite solution, 0.2 per cent. NaOH added, boiled for five minutes, filtered, washed, and dried at 100° C. For other methods see Allen's "Commercial Analysis," vol. iii. (1909 ed.).

2. The "copper" value is determined by boiling 3 g. of the cellulose with 200 c.c. H_2O and 100 c.c. Fehling's solution. The weight of metallic copper calculated on 100 parts of dry cellulose represents the copper value. Hydrocellulose gives 2 to 8.8, oxycelluloses give 7.6 to 35. The copper value gives the number of free carbonyl groups in cellulose, and hence is a measure of its stability. Those sorts of maximum resistance contain no free carbonyl groups (copper value = 0). The oxycelluloses are less resistant to hydrolysis, and hence are less stable and more perishable than normal cellulose.

3. The "ash" and "moisture" in cellulose are determined by the usual chemical methods.

Cellulose Solutions

Cellulose is insoluble in water and simple solvents. Certain metallic salts, however, cause it to combine with water, passing through the condition of gelatinous hydrates into a homogeneous viscous solution.

(*a*) **Zinc Chloride Solution in Water.**—1 part of cellulose is digested in a solution of 4-6 parts $ZnCl_2$ in 6-10 parts water, at a temperature of 60°-100° C. A homogeneous syrup results, which is employed for making lamp filaments by squirting through a fine orifice into water or alcohol. The precipitated hydrated cellulose-zinc-oxide is treated with dil. HCl and well washed.

Vulcanised Fibre for making valve discs, etc., is made by treating sheets of paper with $ZnCl_2$ solution, and subjecting the gelatinised sheet to pressure (see under **Paper**).

Zinc chloride dissolved in HCl (40 per cent.) dissolves cellulose in the cold, but on keeping the solution hydrolyses.

(*b*) **A Solution of Cuprous Hydroxide in Concentrated Ammonia** (cuprammonium solution) gradually gelatinises and dissolves cellulose. The cellulose may be recovered unchanged as a white flocculent precipitate by acidifying with dil. HCl or H_2SO_4.

This property is used in the manufacture of "Willesden" fabrics. Vegetable textiles are passed through a bath of cuprammonium hydroxide, and thus are coated with a film of gelatinised cellulose containing copper oxide, hence the well-known green colour (see under **Paper**).

(*c*) **Viscose or Cellulose Thiocarbonate or Xanthate Solution.**—Bleached cotton, etc., is treated with excess of a 15 per cent. solution of NaOH, squeezed until it retains three times its weight of solution. The soda cellulose obtained is treated in a closed revolving barrel at a temperature of about 15° C., with CS_2, in quantity about 40 per cent. of the weight of the cotton. After about three hours the mass is covered with water, and allowed to stand. On stirring, a crude solution is obtained, from which pure viscose may be made by treatment with brine or with alcohol.

The above reaction may be represented by the typical equation

$$X.ONa + CS_2 = CS.\begin{matrix} OX \\ SNa \end{matrix}$$

Cellulose xanthate.

where X represents the cellulose residue, $C_{12}H_{19}O_9$, or $C_6H_9O_4$. The process is patented by Cross and Bevan (English Patent, No. 8,700, A.D. 1892).

Viscose is reconverted into cellulose (1) spontaneously, on long standing; (2) by heating; (3) by treatment with oxidising agents. This property is taken advantage of in the production of artificial silk or lustra-cellulose (which see), in sizes for paper pulp, for surfacing and finishing paper, and for cloth yarns, for making photographic films, and for agglomerating various filling materials, and finally, in making vehicles for paints. See also **Artificial Silk**, the **Viscose Process.**

(*d*) Cellulose is also dissolved by heating at 180° C. with 7 parts of acetic anhydride, the triacetate, $C_6H_7(C_2H_3O_2)_3O_2$, being produced. The cellulose acetates have now important uses. See under **Cellulose Esters.**

II.—WOOD AND TIMBER PRESERVATION, ETC.

LITERATURE

B. MALENKOVIC.—"Die Holzkonservierung." Vienna, 1906.
P. CHARPENTIER.—"Timber." London, 1902.
NORFOLK CREOSOTING CO., U.S.A.—"Creosoted Timber." 1909.
ANDÈS.—"Feuersicher-, Geruchlos-, und Wasserdichtmachen." Vienna, 1896.
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W. B. CAMPBELL, B.Sc.—"Preservative Treatment of Wood." *Journ. Soc. Chem. Ind.*, 1915, 34, 257.

The chemical constitution of wood has been dealt with under **Cellulose.** For statistics regarding timber, see p. 188.

Treatment of Timber

Timber is very liable to decay, and thus it is that all timber used for constructional engineering is specially treated.

(*a*) **Impregnating.**—Timber to be used for railway sleepers, telegraph poles, etc., is impregnated with antiseptic chemicals, such as creosote oil, zinc chloride, copper sulphate, etc. The wood is dried by stacking for some months; then it is placed on iron bogie frames which are run upon rails into a very strong horizontal iron boiler (say 30-60 ft. long by 6-7 ft. in diameter), which is then closed by a cover. The air is exhausted up to $\frac{1}{3}$ atmosphere so as to remove air from the wood pores, otherwise the air contained in them would resist the entrance of the oil. Next creosote oil * is run in, deeply penetrating into the pores of the wood until the latter is saturated, then a force pump forces more oil into the cylinder until a pressure of 8-10 atmospheres is attained, the pressure being maintained for several hours. The wood absorbs about 1 gallon of oil per cubic foot. This creosoting process is almost exclusively used for telegraph poles, railway sleepers, and piles. Sometimes impregnation is carried out with zinc chloride solution, less often with copper sulphate solution, and now very rarely (on account of expense) with mercuric chloride. Other chemicals used are aluminium sulphate, sodium aluminate, ferrous sulphate, sulphate and borate of ammonium, sodium fluoride, etc. etc.

One of the chief difficulties of creosoting is the presence of moisture in the wood, which impedes the entrance of the oil, because oil and water will not mix. This is the reason why timber after cutting must be "stacked," or air dried, for some months. Vohl proposes to treat green timber by adding enough caustic soda to the creosote to make it miscible with water, impregnating the timber, and "fixing" the creosote with dilute ferrous sulphate. Other attempts consist in making the oils soluble in, or emulsionable with water by sulphonation, by adding soap (0.5 per cent.), zinc chloride, etc. (See German Patents, 139,441, 152,179, 118,101, 150,100.)

The disadvantage of creosoted wood is its great inflammability and smell. Impregnation with metallic salts renders wood almost non-inflammable. Boiling wood with sugar solution for some hours, and drying on hearths, protects wood against mildew and rot, and increases its strength.

(*b*) **Metallisation.**—Here the wood is impregnated successively with two solutions of salt, which combine in the fibres, forming an insoluble precipitate, *e.g.*, the wood is soaked with a soluble copper or zinc salt, and then impregnated with a solution of a resin salt. Insoluble copper or zinc resinates are deposited in the fibres. Similar solutions are: Calcium chloride followed by water glass (Na silicate); calcium chloride + Na_2SO_4; barium sulphide + $FeSO_4$, etc. etc.

* Creosote oil is a coal-tar fraction, of sp. gr. 1.09 at 20° C., distilling between 210°-355° C. It should contain little free carbon.

Gautsche (German Patent, 152,006) renders wood "fireproof" by removing air *in vacuo*, and then impregnating under pressure with ammonium sulphate and borate at 50° C. Such wood will only *char* to a depth of 1 cm., and will not spread fire.

Hasselmann impregnates wood under pressure with boiling solutions of iron and copper salts. Wood is also made fireproof (superficially) by painting with sodium silicate.

(*c*) **Surface-Charring Wood.**—This is an old process, and consists in scorching the surface of the wood with blowpipe flames, and rubbing off the charcoal produced, thus giving a smooth, hard, brown surface, very resistant to moisture and rot. It does not protect the *interior* parts of wood from dry rot should these be infected before carbonisation. The heating of the wood on the surface causes it to be impregnated with tarry matters, and this explains the preserving effect.

(*d*) **Drying Wood.**—Wood is always "seasoned" or air-dried for a considerable time—sometimes two to three years—before being used, by the simple process of stacking under a shed so that air has full access around and between the planks. Imperfectly dried timber will not only easily warp, but is very susceptible to dry rot, mildew, etc. Sometimes, after stacking, the wood is dried in a stream of hot air at 30°-150° C., the wood being placed in large heated chambers for the purpose, and the heating being carried out very gradually, otherwise the wood will split or warp. The dried wood is usually brushed over with tar, linseed oil, paint, etc. "Green timber" contains 40-60 per cent. water, but "air-dry" timber 10-12 per cent. When the moisture content falls below 10 per cent. wood-destroying fungus cannot develop.

(*e*) The **sap** of the tree, containing albuminous matter, sugars, etc., easily becomes decomposed and sets up putrefaction, and nourishes insects, etc. The tendency is lessened by withdrawing the sap, (*a*) by soaking in water, (*b*) better by steaming in enclosed iron apparatus with steam pressure, or simply (but less satisfactory) by sixty to seventy-two hours' steaming in wooden vessels.

Making Wood Non-Inflammable.—The following means are in use:—(1) Painting with water-glass solution; this is probably the best material; (2) impregnating with alum followed by lime, or impregnating with sodium or potassium carbonate, followed by an alum solution; (3) other impregnating solutions, especially for fire-protection, are copper sulphate, zinc chloride, ammonium sulphate and gypsum, borax and magnesium sulphate. See under **Metallisation** above. For methods of making fabrics non-inflammable see Section XVII., Part III., Textile Fibre Industry, p. 527.

III.—WOOD PULP FOR PAPER

LITERATURE

CROSS AND BEVAN.—"Wood Pulp." London, 1911.
MAX SCHUBERT.—"Die Holzstoff oder Holzschiff-Fabrikation." 2nd Ed. Berlin, 1909.
" "Die Cellulosefabrikation." Berlin, 1906.
C. PIEST.—"Die Zellulose." Stuttgart, 1910.
See also the general works mentioned under **Cellulose**, p. 187.

Mechanical Wood Pulp for Paper

The wood blocks, after a preliminary steaming, are pressed against a revolving grindstone, which reduces the material to a fine condition, but not to a powdery form. The disintegrated fibre is pressed against a wire screen, which allows the finer particles to pass through, retaining the coarser particles for further treatment. **Voelter's wood-pulping apparatus** is shown in Fig. 70.

A is the pulping apparatus, with the vat K in which the revolving grindstone S is placed. The blocks of wood are forced against the circumference of the revolving stone by the arms *pp*. Water is introduced at G, and the revolving stone carries the pulp against the screen E, which admits the passage of the finer particles of the wood, while the coarser particles pass away through an oscillating basket placed in the trough into the refining cylinder B, which retains the coarser particles; thence it passes through the distributing apparatus and hopper C to the refining cylinder D. The refining cylinders are covered with fine gauze wire sieves. The ground material which fails to pass through the sieves, is ground up by millstones E, the united pulp being mixed in the tank F, and passed successively from the circumference into the sieving cylinders G, H, and I, thereby removing all coarse particles from the pulp; the rejected coarse particles are ground down by grinding stones and sieved again.

Mechanical wood pulp is only used for making inferior grades of paper, such as news and wrapping, because such paper is difficult to bleach white, and on exposure to sunlight, or on keeping, turns yellow.

The presence of mechanical wood in paper can be easily detected, since such paper gives a purple stain when moistened with a mixture of phloroglucin and hydrochloric acid, while a solution of aniline hydrochloride colours it deep yellow.

The colouring is due to the encrusting matter, the lignin, which surrounds the cellulose fibres of the wood, and forms about 30 per cent. of the wood, the rest being cellulose (60-70 per cent.), resin, and similar products.

Statistics.—The United Kingdom in 1910 imported 8,500 tons of dry and 480,700 tons of wet mechanical wood pulp, of total value £1,160,000. 311,000 tons were obtained from Scandinavia. The United States in 1909 imported 109,000 tons of mechanical wood, value, $2,058,000.

Chemical Wood Pulp (Pure Cellulose)

As mentioned above, ordinary wood fibres do not consist of pure cellulose, but are encrusted with **lignin**, **xylan**, and other complex substances, which cement the cells together into a stiff mass. Ordinary wood contains only about 60-70 per cent. of cellulose, the rest consisting of encrusting substances, resins, etc., all of which must be removed by chemicals before such cellulose can be used for making the better qualities of paper, as the paper otherwise turns yellow and is weak. The encrustations are removed by several methods.

The Sulphite Process.—This is principally used in Scandinavia and Germany, about 560,000 tons of cellulose being yearly manufactured by the

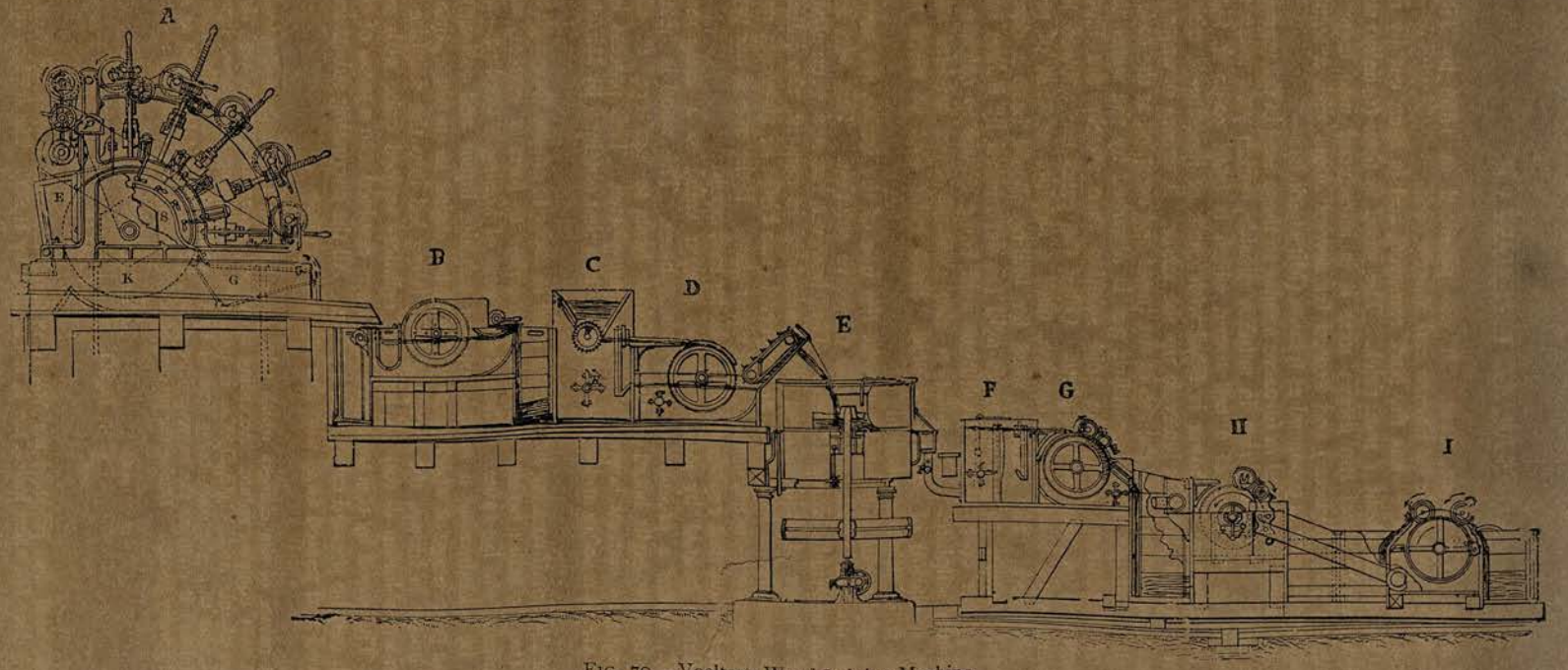

FIG. 70.—Voelter's Wood Pulping Machine.

process (*Z. angew. Ch.*, 1907, 610). It was patented in 1866 by Tilghman, and worked on the large scale by Ekman and Mitscherlich.

The wood—usually pine—has the bark removed, and is then cut by rotating knives into thin slices about 1 mm. thick. The wood is then (usually) steamed, and the brown waste water run away; next it is introduced into large boilers (12 yds. long × 4 yds. diameter) and heated for several hours with a solution of calcium bisulphite, which is produced as follows (Mitscherlich):—

Iron pyrites, FeS_2, is roasted in furnaces similar to those used in the manufacture of sulphuric acid. The gases, rich in sulphur dioxide, which pass away up the flues, are led in at the base of a tall tower, which is from 30-90 ft. high and about 6 ft. in diameter: the tower is filled with chalk or limestones, which rest on a series of gratings placed at intervals up the tower. A stream of water trickles over the limestones, entering at the top of the tower and escaping at the base.

The sulphur dioxide in the ascending gas is absorbed by the water to form a solution of sulphurous acid; the acid solution then attacks the limestone, forming a solution of calcium bisulphite. Often the gases are allowed to pass through several such towers in succession, until a sulphite solution of requisite strength is obtained. The solution used for boiling should have a density of 4°-5° Bé., and contain 30 g. sulphurous acid (as determined by iodine solution) per litre, 25-33 per cent. of the sulphurous acid being united to calcium in the form of calcium sulphite. The solution also contains some calcium sulphate, owing to the oxidation of sulphurous acid. Each cubic foot of wood requires about 1½ cub. ft. of sulphite solution.

Since the sulphurous acid rapidly attacks the iron of the boiler, the latter must be protected on the inside against the corrosive solution. This was formerly achieved by an internal coating of lead. This, however, has now been abandoned in favour of a layer of acid-resisting tiles embedded in cement, the joins being luted with a mixture of lead oxide and glycerol (100 PbO : 12 glycerol), or with a mixture of Chamotte powder, cement, and water glass. If the iron is not protected the corrosion is such that explosions of the boiler may occur.

The boiler is heated by indirect steam (steam coils) to a temperature of 115°-120° C., under a pressure of 2½-4 atmospheres. The wood is heated for twenty-four to forty-eight hours. *Ritter-Kellner* heats to 140°-150° C. with free steam for eight to sixteen hours under 4-6 atmospheres. This process is much quicker, but yields a softer and weaker cellulose than that obtained by Mitscherlich's process.

Occasionally small rotating boilers are used in order to ensure thorough mixing; sometimes two or more boilers are united together to form a system, with the object of utilising the lye twice. When the process of boiling is finished—which is determined by withdrawing a sample of the sulphite liquor and estimating the SO_2 in it, the percentage of which greatly diminishes owing to its absorption by the wood—the boiler is blown, the escaping SO_2 being led into the sulphite towers. Next the brown solution is run off, and the cellulose washed once with water in the boiler. The wood by this treatment has been resolved into a mass of cellulose fibres, which can be pressed easily into a paste. All the encrusting substances have been dissolved and passed away with the sulphite solution.

The exact nature of the changes which take place are not thoroughly understood, being, doubtless, of a very complex nature. According to *Klein* (*Papierzeitung*, 1906, 167), the calcium salt of ligninsulphonic acid, $C_{18}H_{19}O_9SCa$, is produced. According to *Klason*, lignin has a constitution similar to a glucoside, being formed by the combination of aromatic substances and sugars or cellulose: it contains the oxypropylene group, $CH=CH.CH_2OH$, as well as aldehyde, methoxy and hydroxy groups. During the process of boiling the sulphite unites thus:—

$$\begin{matrix} =C \\ \| \\ =C \end{matrix} + H_2SO_3 = \begin{matrix} =CH \\ | \\ =C.SO_3H. \end{matrix}$$

In the compound thus produced the SO_2 is so firmly fixed that it does not exert reducing properties, and does not affect iodine, nor is it liberated by H_2SO_4. The sulphite solution als

contains various sugars, such as dextrose from cellulose, xylose, $C_5H_{10}O_5$, from xylan, tannic acid, resins, proteids, acetic acid, etc.

The cellulose fibres in the boiler must now be carefully freed from twigs, unacted-on wood, knots, dirt, etc., which otherwise would form black specks in the paper. For this purpose it is crushed in special machines, and pulped in Hollanders, the pulp being finally purified from dirt, splinters, etc., by a careful sieving process, the residues being ground up and worked again. Finally the refined wood cellulose is poured on to a wire cloth, as in paper-making, and obtained in the form of thick sheets; it is dried on hot rollers and sent to the paper mills as "**Half-stuff.**" The substance is almost white, but for making the best sorts of white paper it is bleached with chloride of lime and acid, or by electrolytic processes, as is described under **Paper**. This treatment destroys any residual lignin which may still remain in the cellulose pulp. 100 parts by weight of wood yield 40-45 parts by weight of cellulose, the rest going into solution.

Treatment of the Waste Sulphite Lye.—We have just mentioned that over 50 per cent. of the weight of the wood goes into solution in the sulphite lye in the form of the calcium salt of lignin-sulphonic acid, $(C_{15}H_{19}O_9SCa)$, the acid being a gummy body. The lye also contains important quantities of dextrose (from the cellulose), xylose, $C_5H_{10}O_5$, resins, acetic acid, tannins, and gummy matters. It is usually neutralised and filtered from fibres and allowed to run to waste into the rivers, thereby greatly polluting them. Great efforts have been made to find an industrial use for these liquors, the adequate, harmless disposal being an important industrial problem of the present day, and one which is causing increasing anxiety to the large cellulose factories.

In Sweden, the lye is neutralised, and the sugars fermented and worked for industrial alcohol (p. 294).

In several factories the lye is concentrated, when a gummy liquor is obtained which is used as a sizing and finishing agent. The residues forming the black "Cellulose Pitch" have been used for briquettes. By special methods extracts are obtained which are useful in leather manufacture. (See German Patents, Nos. 75,351, 183,415, 194,872, 86,651, 93,944, 93,945, 122,489). The lignosulphite in solution has been used in medicine as a cure for consumption.

The Soda Process.—This process is principally carried on in America, where over 75 per cent. of the cellulose is manufactured by this process. On account of its high cost compared with the sulphite process, and of the evil-smelling gases evolved, the process is only employed to a very limited extent in Europe, principally for **straw**, as the silica encrustations cause difficulties in working it by the sulphite method. The wood, dried and cut up as in the sulphite process, is placed in gas-heated boilers and heated with caustic soda solution of 12° Bé. under a pressure of 6-10 atmospheres. The caustic soda dissolves the lignin, resin, etc. etc., and to some extent attacks the cellulose itself, so that the action is more deep-seated, and the yield less, than in the case of the sulphite process. The soda solution becomes almost black. If straw is to be treated, it is cut up, and heated to 3-5 atmospheres, with a somewhat weaker soda solution than is used for wood.

In either case the cellulose must be carefully washed, resolved into fibres, and bleached before it can be incorporated into fine paper.

The soda lye must be regenerated. It is evaporated *in vacuo* and then calcined, whereby the organic matter is destroyed. The sodium carbonate is extracted by lixiviation with water and is causticised by lime.

In each operation about 10-12 per cent. of soda is lost. The loss is made good by sodium sulphate carbonate.

The "**sulphate**" process is a modification of the soda process, sodium sulphate being the exclusive source of the alkali; this is reduced to Na_2S in evaporating and igniting the lye from the boiled wood. The evil-smelling gases evolved (mercaptans, etc.) are a great objection to the process.

Recently an increased demand has been made for a white "half-stuff" intermediate between mechanical wood pulp and cellulose; the Swedes meet this want by boiling the wood with an insufficient amount of soda for complete action. The product is used in making strong packing papers with a good "rattle," and is known as "**Kraft**" papers.

Cellulose may be manufactured from the refuse fibres of the cotton seed which remain on the seed shells after the cotton has passed through the ginning mill and which are waste products in the process of cotton manufacture. Fats, oils, and

resins are first extracted with naphtha, and the fibres are then boiled with caustic alkaline lye. (See German Patent, 134,263.)

Kellner's Electrolytic Process for preparing Cellulose depends upon the formation of caustic soda, free chlorine, and hypochlorous acid when an electric current of suitable strength is passed through brine.

The boilers A and B, Fig. 71, are charged with wood through manholes D, and then brine is run in until the level rises to the boiler C, as is shown by the water glass E. The temperature is brought to 262.4° F. (117° C.) by steam coils when the current is passed. The gases rise through the apparatus and pass into a condenser G. Every fifteen minutes or so the current is reversed so that alternately the pulp in either boiler is subjected to the action of NaOH and then to the action of Cl and HClO. This process is becoming increasingly popular. (See the French Patent, 326,313, and the American Patent, 773,941.)

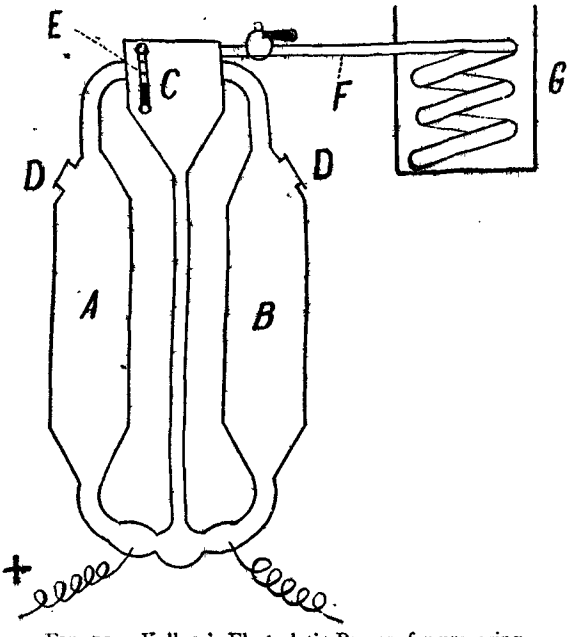

FIG. 71.—Kellner's Electrolytic Process for preparing Cellulose from Wood.

According to **Bühler's Process** (German Patent, 94,467) cellulose is also prepared from wood by treating it with tar oils containing phenols at a temperature over 150° C.

Bleaching Pulp obtained by the above described Alkaline or Sulphate Processes.—Bleaching powder is usually employed, although Na and magnesium hypochlorites are sometimes used, and also, as in the Hermite process, an oxidising solution obtained by electrolysing a solution of $MgCl_2$ or other chloride.

Pure Cellulose may be obtained by boiling cotton, flax, hemp, etc., with a solution of NaOH of about 1-2 per cent. strength, washing, exposing to the action of chlorine gas or bromine water at the ordinary temperature, and again boiling with sodium hydrate, sulphate, or carbonate. Fats and resinous products, produced as by-products during the halogen treatment, are extracted by means of alcohol and ether. The best filter papers are practically pure cellulose. They are treated with hydrofluoric acid to remove mineral matter and leave a minimum of ash.

The Wood Cellulose obtained by the various processes above described consists of a soft mass of fine fibres (Fig. 73), each fibre being made up of an elongated cell somewhat resembling that of a cotton fibre, but much shorter (3-5 mm. long against 20-70 mm. for cotton).

Fig. 72 shows wood cellulose fibres—1 and 2 representing cells magnified to different degrees, while 3 represents a section. It will be seen that the fibres are hollow, with pointed ends, and provided with a number of minute pores *a*, *a*, *a* running right through the cell walls. See 4, Fig. 72, for a section through a pore.

Statistics.—In 1910 England imported 350,000 tons of **dry** and 20,000 tons of **wet** chemical wood pulp, of total value £2,340,000. Of this, no less than 299,000 tons came from Scandinavia.

The United States *imported* in 1909, 157,000 tons (value $6,600,000), and in 1910, 234,000

tons (value $9,200,000). The export was 9,200 tons (value $449,000) in 1909, and 7,900 tons (value $360,000) in 1910.

Wood-Cellulose Cloth and Yarn.—Attempts have frequently been made to spin the cellulose pulp into cloth, but the fibres have always proved too short. The firm *Altdamm* near Stettin, however, appears to have solved the problem by forcing the pulp through narrow gutters, and then converting the narrow flat ribbons thus produced by a rolling motion into spinnable fibres. Ropes, cloth, and even clothes have been thus made from paper pulp. The dry cloth is fairly strong, but the wet is very weak.

The yarns are placed on the market under the names silvalin, xylolin, licella fabrics, etc., and form a cheap substitute for cotton and flaxen yarns. (See German Patents, 136,371, 142,678, 149,444, 159,418, 167,490.)

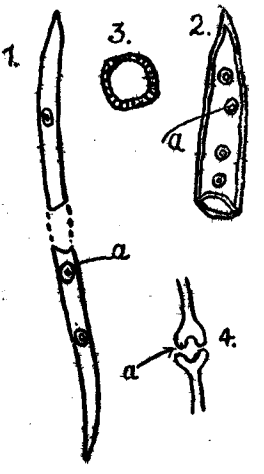

FIG. 72.—Cellulose Cells (Wood Fibres)—(1) Fibre; (2) the same enlarged; (3) section of 2; (4) section of wall or cell through a pore; *a*, *a*, *a*, pores.

Hydrocellulose, $C_{12}H_{22}O_{11}$, is manufactured on the large scale because it yields a gun-cotton more readily exploded by concussion than ordinary gun-cotton. The process is as follows: Pure cotton is immersed for three or four minutes in a solution of 3 parts of concentrated H_2SO_4 or HCl in 97 parts of water. The cotton is freed from adhering liquor, dried, heated at a temperature of 104°-158° F. in stoneware vessels for three to ten hours, washed, and again dried.

Another process (German Patent, 123,122) treats cellulose with a small amount of $KClO_3$ and HCl, keeping the temperature at 60°-70° C. It forms a white powder, not very sensitive to acids or alkalis, and so is used for making acid proof or alkali-proof articles. When the mixture is treated with S_2Cl_2, and the product poured into water, a sulphur-hydrocellulose is produced (German Patent, 137,206), which can be used for vulcanising rubber, both the cellulose and sulphur combining with the rubber.

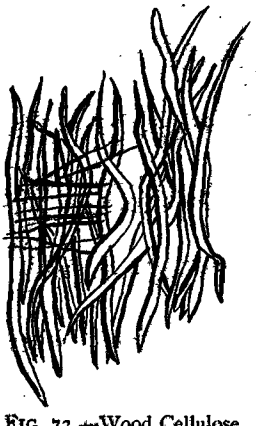

FIG. 73.—Wood Cellulose Fibres.

Oxycellulose, $C_9H_{10}O_6$ or $C_6H_8O_6$, is obtained by the action of mild oxidising agents on cellulose, *e.g.*, by treating cotton with NaOH + dil. $KMnO_4$ solution $\left(\frac{N}{10}\text{ solution}\right)$, or by boiling filter paper with two and a half times its weight of dil. HNO_3 (sp. gr., 1.3). Several kinds of oxycelluloses are known. They are used for obtaining a damask effect in the cotton industry.

Hydrocellulose and oxycellulose both readily reduce Fehling's solution, and are thus distinguished from normal cellulose.

IV.—PAPER-MAKING

LITERATURE

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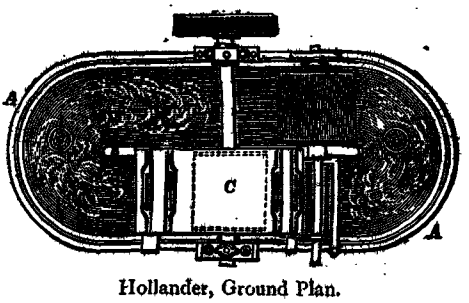
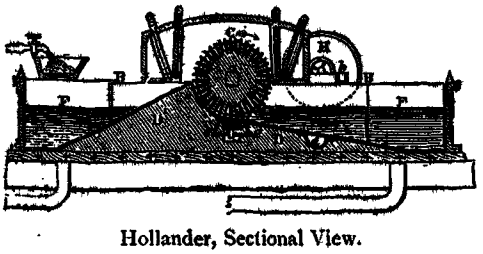
The Materials used consist of linen rags, esparto grass, wood-pulp, mechanically powdered wood, etc. etc. The bulk of paper produced is made from wood and esparto. After the materials have been well boiled with soda or other cleansing chemical to free them from dirt and extraneous matter, the crude product is next transferred to a cutting or pulping engine called a "Hollander." It consists of a cast-iron trough A, Fig. 74, about 10 ft. long, 4½ ft. wide, and 2½ ft. deep, rounded at the ends. It is provided with a partition called the *midfeather* BB, of such a length as to have the trough of uniform width round it. A cylinder or *roll* C, furnished with a series of steel knives, rotates in one of the divisions formed by the midfeather; the floor of the trough in this division is inclined in such a manner as to cause the pulp as it travels to pass under the roll. If the machine is to be used for cutting rags or similar material (not grass) a *bedplate* is placed beneath the roll; this is fitted with a series of steel knives similar to those on the exterior of the roll. The distance between the knives of the roll and the bedplate is regulated by levelling screws, so that the material may be cut to any required degree of fineness. The drum washer H is covered with fine wire gauze or cloth, and allows water to run away (or enter) without any of the pulp fibres passing out with it.



Hollander, Ground Plan.



Hollander, Sectional View.

(See also Fig. 244, p. 628.)

FIG. 74.

The object of the knives is not so much to shorten the fibres by cutting—as this would weaken the resulting paper—but to draw them

apart and separate them. The material is worked in the hollander until cut up into the necessary fine state of division, when it is known as "**Half-stuff.**"

The half-stuff is run from the hollander into a mixing engine called the "potcher," or "poacher," where it is agitated with the necessary quantity of bleaching liquor, chloride of lime and dil. HCl or H_2SO_4 being usually employed, although in recent years processes of electrolytic bleaching are coming into use.

From the bleaching apparatus the half-stuff is now run into a "beating engine." This is similar to the hollander previously described, but the knives of this engine are more numerous, and revolve more rapidly. This machine achieves the purpose of washing the half-stuff free from bleaching material and acid, and reducing the half-stuff to a slightly finer state of division necessary to make the fibres "felt" (*i.e.*, intertwine) well together on the shaking wire of the paper machine. It also serves as a mixing engine for loading, sizing, and colouring the paper pulp before actually making it into paper.

Before sizing, the last traces of chlorine are removed by treating the pulp with "antichlor." For this purpose sodium thiosulphate is usually employed, which decomposes any bleaching powder still in the fibre, thus :—

$$\underset{\text{Bleaching powder solution.}}{2Ca(OCl)_2} + \underset{\text{Sodium thiosulphate.}}{Na_2S_2O_3} + H_2O = \underset{\text{Calcium sulphate.}}{2CaSO_4} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Sodium chloride.}}{2NaCl.}$$

Sodium sulphite is now largely used for the same purpose :—

$$\underset{\text{Bleaching powder solution.}}{Ca(OCl)_2} + \underset{\text{Sodium sulphite.}}{2Na_2SO_3} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Sodium chloride.}}{2NaCl.}$$

Although three times as much of sodium sulphite is required to produce the same effect as a given amount of sodium thiosulphate, yet the sulphite is preferred by paper-makers, as no free acid is formed, which would corrode the wire of the paper-making machine. Hydrogen peroxide also produces excellent results, but is too costly. The presence of bleaching powder in the stuff is determined by testing with KI + starch solution. The chlorine sets free iodine, which colours the starch blue. Hence the addition of antichlor to the pulp is continued until the latter ceases to give a blue stain with KI + starch solution.

Sizing.—Unsized pulp, as it comes from the bleaching tank, is bibulous, and if made into a paper with the addition of a little starch as binding material, forms what is known as "blotting paper." Such paper is very weak. Writing or printing paper must be "sized" so that they acquire a water and ink resisting quality.

Engine sizing (Rosin-alum-sizing) is used for writing and wrapping papers. When rosin—which is abietic acid, $C_{44}H_{64}O_8$, or its anhydride—is heated with a solution of alkalies it rapidly dissolves, forming rosin soaps.

$$C_{44}H_{64}O_8 + Na_2CO_3 = C_{44}H_{62}O_8.Na_2 + CO_2 + H_2O.$$

100 parts of rosin require 15-18 parts of sodium carbonate to form a "neutral" rosinate. Sometimes starch solution is added. The rosin soap is now added to the paper, 100 lbs. paper requiring 3·4 lbs. of the original rosin. Then after thorough mixing a solution of **alum** or aluminium sulphate is added, and this decomposes the sodium rosinate, the insoluble aluminium rosinate being precipitated thus:—

$$\underset{\text{Sodium rosinate.}}{3Na_2C_{44}H_{62}O_8} + \underset{\text{Aluminium sulphate.}}{Al_2(SO_4)_3} = \underset{\text{Sodium sulphate.}}{3Na_2SO_4} + \underset{\text{Aluminium rosinate.}}{Al_2(C_{44}H_{62}O_8)_3.}$$

100 parts rosin should, theoretically, require 23 lbs. of alum—as a matter of fact, over three times as much is used. The aluminium rosinate precipitated in the paper pulp was supposed to be the sizing agent, which makes the paper non-absorbing of ink. C. Wurster concludes that the *effective* sizing agents are *free* rosin acids (since paper extracted with ether loses its water-resisting properties with the removal of the free rosin acids), and the function of the *excess* of alum is to decompose the neutral rosinate of alumina with liberation of the free acid, thus :—

$$Al_2R_3 + 2Al_2(SO_4)_3 + 3H_2O = \underset{\text{Free rosin acid.}}{3R.H_2} + \underset{\text{Basic sulphate of alumina.}}{3Al_2O(SO_4)_2.}$$

R stands for $C_{44}H_{62}O_5$, the radicle of abietic acid, $C_{44}H_{62}O_5H_2$.

Among auxiliary agents used in sizing may be mentioned **starch**, alumina, soap, and cellulose hydrates. The latter constitutes viscose sizing (see under **Viscose**), the viscose being added to the pulp, mixed, and decomposed by adding zinc or magnesium sulphate. The fibres thus become coated with a film of **gelatinous** cellulose, which exerts a powerful cementing action in making and drying. Such paper is very strong, but the process does not seem to have been adopted to any large extent.

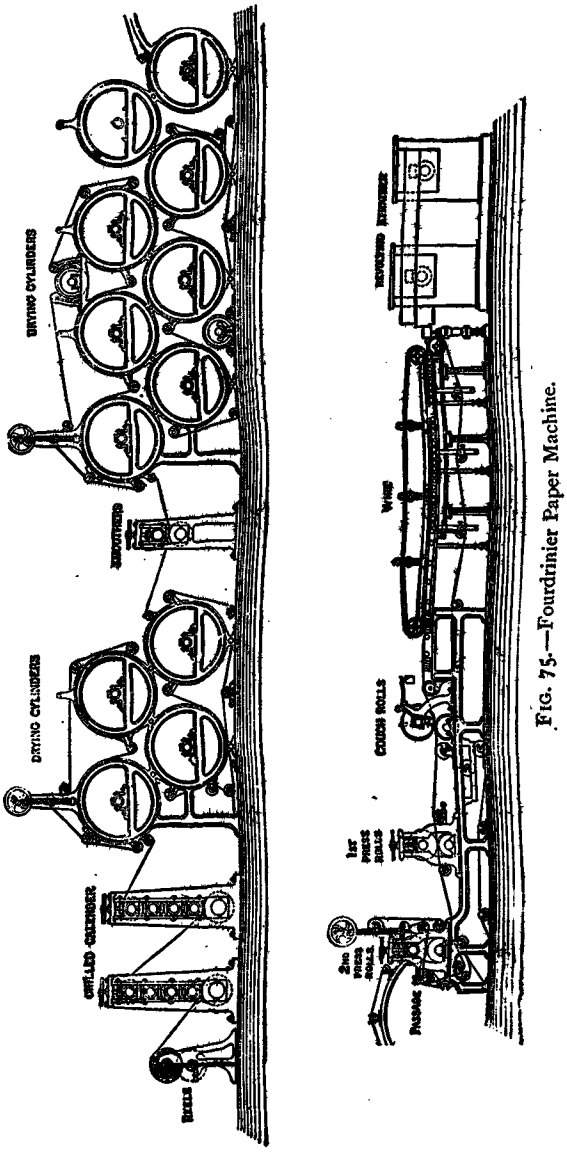


FIG. 75.—Fourdrinier Paper Machine.

Silicate of Soda and **Casein**—the albuminoid substances contained in milk—are also sometimes used in sizing. Casein is coming more into use, being added to the pulp in the form of a strong solution, which is completely precipitated by alum; it imparts toughness and a good "handle" to the finished paper. Sometimes the casein is mixed with sodium silicate.

If the sizing takes place after the conversion of the material into paper (surface sizing), animal size alone is used.

Mineral Filling and Loading Agents.—It is usual to add to the pulp a quantity of a cheap mineral loading material to make the paper more suitable for the particular purpose to which it is applied. **Kaolin** or **china clay** is the loading usually employed in making **news, printing**, and low-grade writing paper. The clay is added to the pulp after making into a cream with water. The addition of clay serves to fill up the pores of the paper, giving a smoother surface and increasing its absorbent power for printing ink, and also gives an improved surface in calendering. It also adds to the opacity of the paper.

For the better qualities of writing papers the materials used are calcium sulphate ("pearl hardening"), barium sulphate, barium chloride, and **agulite**, a fibrous-like mineral like asbestos.

Starch is always applied to papers in the process of manufacture, for the same reason that it is used in laundries for preparing collars and cuffs, viz., to give it a fine polish and hardening effect in the subsequent glazing process, when the paper is passed through hot iron rolls.

Colouring.—The bleached pulp has always a yellowish tint. This is removed by mixing in **blue** ultramarine, smalt, or similar "correcting" colour, a pure white-looking paper then resulting.

The colouring of paper is either effected by grinding suitable pigments into the pulp or using suitable aniline colours for dyeing the pulp.

Paper Machines.—The pulp is now ready for making into paper. The pulp, properly sized, loaded, and coloured, is discharged from the mixing engine, through strainers, into the paper-making machine, usually known as the **Fourdrinier.** (See Fig. 75.)

It consists of an endless wire-cloth from 32-50 ft. in length and almost any width up to 126 in., travelling at the rate of 100-300 ft. per minute. The wire-cloth is made of exceedingly fine wire, the meshes ranging from sixty threads upwards to the inch. The pulp, after it leaves the beating engine for conversion into paper, passes first into large cylindrical vessels known as "stuff-chests," containing rotating arms to keep the pulp and water intimately mixed. Thence it runs into straining machines, and thence into a vat provided with a horizontal agitator; from the vat it flows on to the endless wire-cloth of the paper-machine. The wire-cloth is

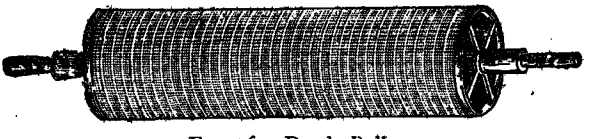


FIG. 76.—Dandy-Roll.

supported by a series of brass tube rolls, carried upon brass bearings, and motion is given to it by the rotating couch-roll at the end. When it is required to produce a design or name, called a *water-mark*, upon the paper, this is done by means of a roll called the *dandy-roll*, which consists of a skeleton roll covered with wire-cloth, upon which the design is worked by means of very fine wire. At the extreme end of the wire-cloth, and inside the wire, is the *under couch-roll*, from which the wire receives its motion. Above this is the *upper couch-roll;* both rolls are covered with felt, the upper roll resting upon the lower one. The wire-cloth with the web of paper upon it passes between the rolls, receiving gentle pressure, by means of which the paper becomes deprived of much water, rendering the paper compact. Here the web of paper leaves the wire-cloth, and passes on to a continuously revolving and endless web of woollen felt, called the "wet felt," about 20 ft. long and carried on wooden rollers. The paper then passes to the *first press-rolls*, which deprives it of a further quantity of water; the surface of the paper is then reversed in the *second press-rolls*, so that both sides of the paper are brought into the same condition. From the press-rolls the paper passes to the drying cylinders, which are heated by steam. The paper slowly passing over their surface is dried and brought into a proper condition for passing between the *smoothing-rolls*, also heated by steam, which give the paper a fine smooth surface. The paper then passes over another series of drying cylinders, where it is perfectly dried. The paper now passes through the *calender rolls*, hot polished rolls, where it receives a fine glaze; finally it is wound on to the reels at the extreme end of the machinery. The paper is then cut by special machinery into sheets of any required dimensions.

The strength of paper is largely determined by the length of the fibres—the longer the fibres the stronger the paper.

Wood cellulose is now one of the most important materials for paper-making. Cheap printing papers contain 50-80 per cent. of mechanical wood pulp. The better qualities of writing paper consist of pulped linen rags. The best and most permanent sorts of paper—such as employed for legal documents—are made of pure linen or hemp fibres.

Parchment Paper, which is extensively used for covering jars and pots for pickles and jams, and for binding books, is made by dipping white unsized paper for a few seconds into concentrated sulphuric acid and washing free from acid with dilute ammonia. The cellulose has been turned by this treatment into a hydrocellulose, and is impervious to grease, water, etc. Coloured parchment paper is used as a leather substitute.

The conversion of cellulose into gelatinous hydrocellulose can also be effected by the wet-milling processes employed by the paper-maker. Thus a "*grease-proof*" *imitation parchment paper* is obtained by pressing, crushing, and rubbing the fibres for a long time in the presence of water, *wood sulphite cellulose* being usually ground up in a special Hollander provided with blunt knives. Ultimately the cellulose absorbs water and a slimy mass is obtained, which makes the translucent paper so largely used as a packing for butter, sausages, and other provisions, since it is impervious to fat. This paper has no loading or sizing material, with the exception of a little starch, and is strongly calendered. If such paper is warmed over the point of a small candle flame tiny bubbles appear—due to steam which cannot escape through the water-tight surface of the paper. This is used as a test for its fat-proof quality.

"**Cellulith**" is obtained by carrying the mechanical hydration to its fullest extent. The cellulose is ground with water for 40-150 hours, when the fibrous structure is completely broken down, with the production of an amorphous cellulose jelly. This is boiled for two hours to expel air, and then hardens on drying to a product of the consistence of bone. This mass can be mechanically worked and polished like horn, bone, or ebonite, and is used as a binding-agent for carborundum or emery wheels, and as a packing-material for making tight the covers of autoclaves, etc. It withstands the action of alcohol, ether, petroleum, fats, and oils.

Waterproof Papers are usually made by passing paper through a cellulose solvent, such as copper hydroxide dissolved in ammonia (cuprammonium). The fibres are cemented together by the solvent action of the cuprammonium, and when dried acquire a varnish-like surface. A strong solution of zinc chloride acts in a similar way. Sheets of paper treated with concentrated zinc chloride solution are placed one on the other and pressed or rolled by hot rolls into thick homogeneous solid plates resembling thick sole-leather. Paper treated in this way is known as "vulcanised fibre" and is made pliable by soaking in glycerin. It is used as a water-tight isolating and packing material, for pumps, etc. etc. Such blocks may be bored, turned, polished, and coloured. (See Marshall, *Ch. Z.*, 1908, Rep. S. 544. Also Piest, "Die Zellulose," Stuttgart, 1910.)

Papier-Maché is made of paper pulp and binding materials, the mass being moulded. Some sorts are made by cementing together sheets of paper. A flexible, impenetrable, and acid-proof composition is obtained by moulding a pulp made of 15 per cent. rags and 85 per cent. cellulose, drying by hot air, steeping in solutions of resin oils, drying, and again steeping.

Cardboard may be made like paper, by pouring the pulp on to wire frames until it is thick enough. The product is weak. The better sorts are made by pressing moist, quite freshly-made sheets of paper one on the other. They adhere under pressure, and form a solid mass called "couched pasteboard." Carton pasteboard is made by pasting finished and dried leaves of paper one over another till the proper thickness is attained. Sometimes tar and crushed stones, asphalt, etc.,

are mixed into the paper pulp for making roofing or tar pasteboard. **Carton Pierre** for roofing is made this way.

Testing Paper.—The mechanical tests for paper (strength, etc.) are usually carried out with special apparatus, which are described in Allen's "Commercial Organic Analysis," vol. i. p. 467.

The Ash is determined by drying 1-2 g. to constancy at 100°-105° C., and igniting in a platinum (or porcelain) crucible until the weight is constant. If the paper contains lead compounds, this will attack the platinum, and the determination must be carried out in a porcelain crucible. A qualitative analysis of the ash reveals the mineral loading-agents used.

The **presence of Mechanical Wood** is shown by moistening with (1) a solution of phloroglucinol acidified with HCl, which gives a purple colour with wood; or (2) aniline sulphate solution, which gives a yellow colour with wood.

The **Sizing** is tested by *Leonhardi's* method: the paper is moistened with one drop of a 1.5 per cent. ferric chloride solution for as many seconds as the weight of the paper in grams per square metre. Then the paper is dried with blotting-paper, and the back is painted with a 1 per cent. tannin solution. With well-sized papers no coloration should take place, badly sized papers colour almost immediately, moderately sized in about sixty seconds. Rosin in the size is detected by boiling with absolute alcohol + a little acetic acid, and a milkiness is produced on pouring into water, or by extracting paper with **ether** and evaporating, when a layer of rosin is left.

Animal Size (glue, gelatine) is detected by boiling the paper (10 g.) with a little water, filtering, evaporating to small bulk, and adding tannin solution. A greyish precipitate, *not turned blue* by I + KI solution, shows animal size. Starch also gives a precipitate with tannin, but this is turned blue by the iodine solution.

The **fibrous** constituents of paper are usually determined by a microscopic examination; the application of certain staining chemicals also helps to differentiate between them. The following table shows this:—

Fibres.	Iodine Solution.	Zinc Chloride + Iodine Solution.	Magnesium Chloride + Iodine Solution.
Mechanical wood pulp, jute, straw (partially boiled), unbleached manilla.	Yellow.	Yellow.	Yellow.
Cotton, linen, hemp	Brown.	Claret.	Reddish brown.
Esparto, straw, bamboo	Grey or greyish brown.	Blue to violet.	Bluish violet.
Wood cellulose	Colourless.	Blue or violet.	Brownish or red.
Manilla hemp	Yellowish brown or grey.	Yellow.	Yellow.

Statistics.—548,000 **tons** of paper, of value £6,410,000, were imported into the United Kingdom in 1910. The export was 144,000 tons, of value £3,140,000. The composition of the paper-making materials imported in 1910 is shown by the following figures:—

PAPER-MAKING MATERIALS IMPORTED INTO THE UNITED KINGDOM IN 1910

	Tons.	Value.
Linen and cotton rags	18,500	£201,000
Esparto and other vegetable fibres	193,000	666,000
Chemical wood pulp	351,000	2,837,000
Mechanical wood pulp	488,000	1,225,000
Other materials	14,000	102,000

The United States in 1910 *imported* paper and paper manufactures to the value of $3,390,000. The following figures give the *exports*:—

	1906.	1910.
Books, maps, printed matter	$5,839,000	$7,089,000
Paperhangings	311,000	297,000
Playing cards	258,000	222,000
Printing paper	3,667,000 (138,856,000 lbs.)	2,767,000 (92,738,000 lbs.)
Writing paper	$976,000	$1,267,000
All others	4,374,000	4,442,000

The paper-making materials *imported* into the United States is given by the following figures:—

	1910.	Value in 1910.
Rags	180,114,000 lbs.	$2,167,000
Wood pulp	847,441,000 ,,	11,768,000
Other paper stock	...	3,039,000

V.—MERCERISATION

LITERATURE

"Mercerisation." A practical and historical manual by *The Dyer and Calico Printer*. London, 1903.

GARDNER.—"Die Mercerisation der Baumwolle." Berlin, 1898.

ICHENHÄUSER.—Article "Mercerisation" in Dammer's "Chemische Technologie der Neuzeit." Gives recent patents.

Cotton fibre when brought into contact with sodium hydrate solution containing more than 10 per cent. Na_2O changes from a hollow flattened riband to a thickened cylinder with practically no hollow. This effect is seen in cotton cloth as a shrinking in length and width accompanied by a thickening in substance, and is known as mercerisation, after the inventor Mercer (1844). Cloth so treated is stronger, and has an increased dyeing capacity. By acting on cloth weaved of a mixture of cotton and wool, the wool is unaffected, while the cotton shrinks up, causing a relief crépon effect.

Mercerisation is effected in two ways :—

1. The caustic soda (20-25 per cent.) is allowed to act on the cloth or yarn when stretched in frames, thus forcibly preventing any longitudinal shrinking of the fibres; the latter retain their original length and strength, but simultaneously acquire a beautiful silk-like lustre when the caustic soda is removed by washing.

2. The cotton is soaked in a solution of caustic soda, squeezed or centrifuged

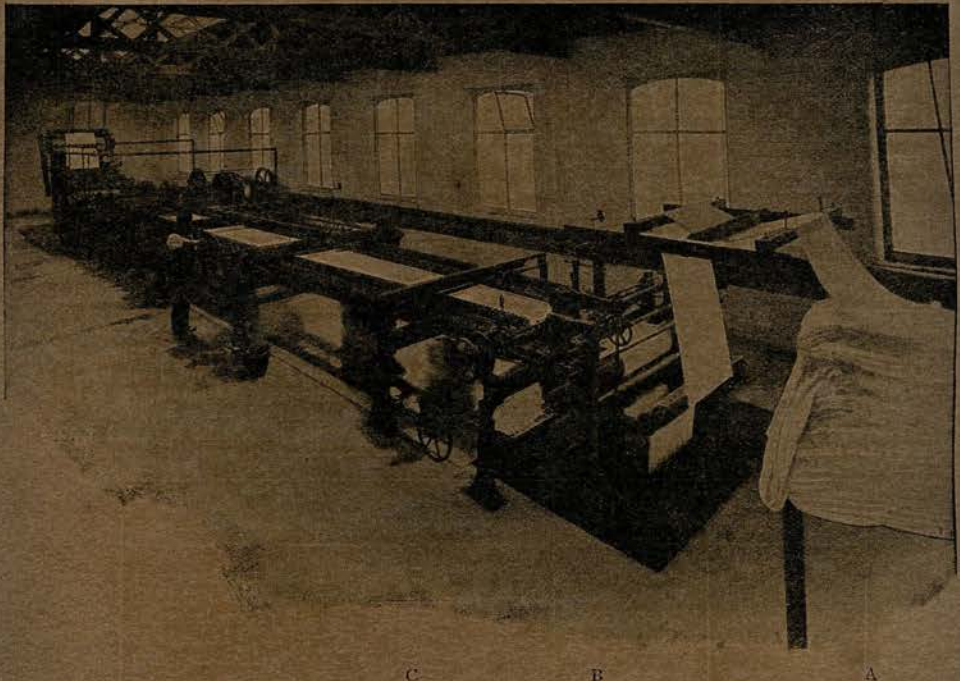


FIG. 77.—Mather & Platt's Mercerising Range.

to get rid of excess of moisture, stretched a little beyond its original length, and washed while still in a state of tension to remove the NaOH.

Mather & Platt's apparatus for mercerisation is shown in the illustration (Fig. 77). The cotton fabric A first passes into the caustic soda tank B in the foreground, where it is twice soaked and twice squeezed dry by rollers placed inside; the goods then pass into the tension frame C, where it is stretched the proper amount, and afterwards in the second part of the apparatus D the caustic soda is removed by washing with warm water issuing from a central perforated pipe laid above the cloth, the wash water running away being caught and evaporated so as to regain the soda. On issuing from the tension frames the material passes in order through a washing-tank E, squeezing-rollers, an acid-tank, squeezing-rollers, and a couple of massive rollers F where it is strongly compressed; the cloth is then laid in folds as it issues from the machine. A section of Sir James Farmer's Mercerising Range is also shown in Fig. 78.

The strength of the cotton is increased by mercerisation 68 per cent. if unstretched, and 35 per cent. if stretched (Buntrock, *Z. Angew. Ch.*, 1898, 982).

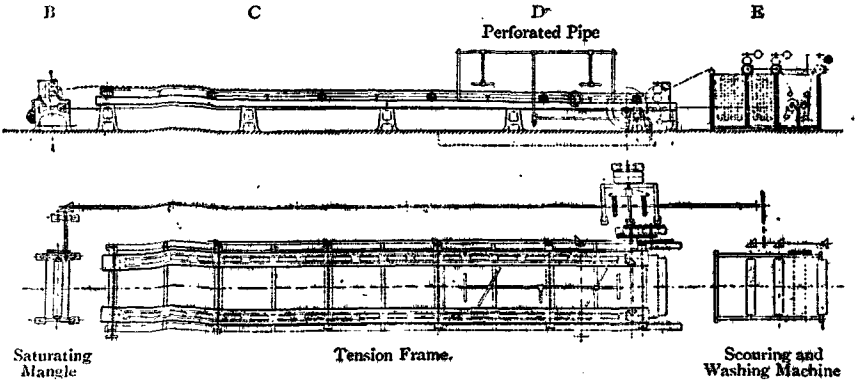


FIG. 78.—Section of Sir James Farmer & Sons' Mercerising Range.

The silky finish is especially marked when long-fibred sorts of cotton are employed, and is intensified by subjecting the mercerised material to a special calendering-process. Beautiful crépon effects are obtained by locally mercerising stretched cloth—the NaOH being prevented from spreading into neighbouring parts of the cloth by first printing the parts with gummy material; the caustic soda is then only able to mercerise those portions of the cloth not covered with gummy material. This process has now attained great industrial importance.

As far as the chemistry of the process is concerned it is thought that cellulose when treated with the NaOH forms the compound $(C_6H_{10}O_5)_2Na_2O$, which on washing decomposes into the cellulose hydrate $(C_6H_{10}O_5)_2.H_2O$.

Tests.—To distinguish between mercerised and non-mercerised cotton a microscopic examination is necessary. *Lange* advises treating the sample with a cold saturated solution of $ZnCl_2+KI+I$ (*e.g.*, 30 g. $ZnCl_2+5$ g. $KI+1$ g. I in 24 c.c. of water). Such a solution gives a *blue* colour to both mercerised and non-mercerised cotton. On rinsing with cold water the colour *persists* with *mercerised cotton*, and *disappears* with non-mercerised. If the cotton is coloured it must be bleached before applying the test.

VI.—COLLODION

Collodion is a weakly nitrated cellulose, usually regarded as a dinitro-cellulose, $C_6H_8(NO_2)_2O_5$,* containing 10-11 per cent. N, and easily soluble in a mixture of alcohol and ether (2 : 1). Several such dinitro-celluloses exist,† some soluble and some insoluble, and it is usual to distinguish between those intended for the manufacture of blasting-gelatine and nitroglycerin powder and those for making celluloid and for artificial silk. Usually the cotton wool is purified by treating with soda (wood cellulose requires such energetic purification that it is not used for the manufacture of nitro bodies), and then 1 part of cotton is nitrated with 20 parts H_2SO_4 + 9 parts KNO_3. The cotton wool is left in the acid mixture until a sample, when withdrawn and crushed, will dissolve in a mixture of alcohol and ether (2 : 1). The temperature during nitration must remain low. The collodion wool (dinitro-cellulose) is washed with cold water, then with boiling water, and is carefully stabilised, as described under **Gun-cotton** (see **Explosives**, p. 624). It is sometimes stabilised by heating when wet with dry superheated steam. The solution in alcohol-ether is also known as **Collodion**. It dries to a colourless elastic skin. Collodion is principally used in photography and medicine, for varnishes, films, and for impregnating incandescent mantles.

England imported 87 gals. in 1910, value £76. The United States in 1910 imported 84,500 lbs. (value $335,900).

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* On Eder's formula, $C_{12}H_{16}(NO_2)_4O_{10}$ (tetranitrate), and on Vieille's, $C_{24}H_{32}(NO_2)_8O_{16}$ (octo-nitrate); Vieille's more closely represents the facts.

† See p. 628.

VII.—CELLULOID, XYLONITE, ETC.

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Moniteur Scientifique, 1908, p. 648. Article on "Derivés Plastiques de la Cellulose et de les composes."
See also under **Celluloid Substitutes.**

Celluloid consists of a low-nitrated cellulose, usually termed pyroxylin, and camphor, and was discovered by Alexander Parkes about 1860, and by the brothers Hyatt of Newark in 1869. These substances, when pressed together and warmed, unite to form a transparent substance, which is not explosive and which possesses properties very different from the component bodies. The nature of the union is unknown, but it is believed that a "solid solution" and not a definite compound is formed. Several processes exist for effecting the union, but they may be divided into two types:—

1. **The Dry Process.**—The well washed and dried pyroxylin is ground up as finely as possible under water in a Hollander (see **Paper-making**), the water is removed, and the mass is subjected to a very great pressure in a perforated vessel. Next, the mass is mixed with 40-50 per cent. of camphor, well kneaded and mixed in special machines and at the same time *colouring* matters and other products mixed in. The mass is now subjected to very great hydraulic pressure, and at the same time heated by steam to about 130° C. The nitrocellulose rapidly dissolves in the melted camphor, and celluloid is produced. After remaining in the press for some hours the celluloid is dried in a vacuum over $CaCl_2$. Hyatt's original method is a modification of this.

2. **The Wet Process.**—In the alcohol and ether process of Magnus & Co., 50 parts of pyroxylin are placed in stoneware vessels and 28 parts of camphor dissolved in 100 volumes of ether and 5 volumes of alcohol are added, and the whole, together with a "stabiliser" or "antacid," such as urea, stirred up in the closed vessel (to prevent evaporation of the ether). The crude plastic stuff so obtained is rolled out into sheets, and after hardening is treated in a warm state in the hydraulic press. The process is only suitable for the production of moderately thin sheets or bars of celluloid. The danger of explosion and fire through the use of ether vapour is very considerable. Best uses methyl alcohol instead of ether for dissolving the camphor.

Celluloid is a horn-like, semi-transparent, or even transparent, body. It is hard, very tough, and elastic. Inferior qualities smell of camphor, the best sorts are odourless. It is insoluble in water, and when hot can be welded and moulded. At 125° C. it becomes plastic; at 140° C.-145° C. it decomposes without explosion It is extremely inflammable, burning with a smoky flame, and emitting a camphor like smell. Celluloid cannot be made to explode by heating, friction, or a blow.

Since camphor is dear a large number of substances have been proposed in its place for making celluloid. Thus we may mention **acetine, methyl naphthyl-ketone, dinaphthylketone, naphthalene, naphthalene acetate, nitro-naphthalene, halogen derivatives of the aromatic hydrocarbons, esters of phenol, cresol, naphthol, etc. etc.** The use of the carbonates of the phenols, cresols, and naphthols is suggested in the German Patent, 139,589; the use of **borneol** is suggested in the English Patent, 11,512, 1905. The English Patent, 5,280, 1904, suggests the use of mixed ketones, while the English Patents, 17,948, 1900, and 8,072, 1901, use the phenol ester of phosphoric acid.

The great disadvantage of celluloid is its inflammability, and many methods have been proposed for diminishing this, such as the addition of mineral fillers, such as asbestos, magnesium chloride, aluminium salts, etc. Organic compounds of silicon have been recommended (English Patent, 10,320, 1910) as fillers. It has also been proposed to use in place of the very inflammable nitrate other esters of cellulose. See next Section.

Statistics.—England imported celluloid ware to the value of £450,000 in 1910; xylonite and celluloid ware to the value of £167,000 were exported. The United States exported celluloid to the value of $1,189,000 in 1910; $341,000 in 1906.

VIII.—CELLULOID SUBSTITUTES, ARTIFICIAL BONE, HORN, IVORY, AND SIMILAR PRODUCTS

LITERATURE

See under works on **Celluloid**; also S. LEHNER, "Die Imitationen" (Vienna, 1909); J. HOFER, "Die Fabrikation künstlicher plastischen Massen" (Vienna, 1908); R. SCHERER, "Casein" (London, 1905); also an article in the *Moniteur Scientifique*, 1909, vols. 70-71, p. 157, "Etat Actuel de l'Industrie des Matière Plastiques Artificielles." For artificial **Horn, Resins, and Shellacs** see the *Journal of Industrial and Engineering Chemistry*, vol. i. (1909), pp. 149, 545; *Transactions of the American Electro-Chemical Society*, vol. xv. (1909), p. 597. See also Patent Specifications referred to in text below.

(*a*) **From Cellulose Acetate**, etc., non-inflammable **celluloid substitutes** are made by mixing cellulose acetate, formate, or double esters, such as the sulphacetates and phosphacetates (the latter being more readily soluble in cheap solvents), with camphor or its substitutes. The so-called "**cellite**" films for kinematographs are made in this way, and are only with difficulty inflammable. Combs, toys, balls, etc., of this "cellite" are now manufactured and used as a substitute for the inflammable and even dangerous celluloid. (See English Patents, Nos. 26,075, 1901; 7,088, 1902; 1,441, 1910.)

Horn-like bodies are obtained from cellulose acetate by heating with mono- or polyhydric phenols, chloral hydrate, thymol and chloroform, castor oil and $CHCl_3$, or phenol alone under pressure (German Patents, 145,106, 151,918, 152,111; American Patents, 774,713 and 774,714; English Patent, 9,537, 1907).

Cellulose Formate is used in English Patent, 2,511, 1907, and **Compound Cellulose** esters in English Patents, 27,102, 1909; 8,646, 1910; 29,246, 1910. (See under **Cellulose Esters** for manufacture of cellulose acetate, etc.)

(*b*) From **Casein or Milk Curds** (see **Industrial Casein**, p. 79).

Galalith is the best known horn or celluloid-like substance obtained by the action of formaldehyde on **casein** (from milk). The casein is dissolved in alkalies (such as caustic soda or aqueous ammonia), and the clarified solution is precipitated with acids, filtered, pressed, and dried slowly during some weeks or months. The plates so obtained, when soaked in formaldehyde and dried, form a yellowish white translucent product, very tough like horn or ivory. It may be coloured or marbled by adding dyes, soot, cork powder, etc., to the casein solution before precipitation. Galalith has a sp. gr. 1.31-1.35, is moderately hard (2.5 Mohr), is a good electric insulator, can be cut and worked cold, and when warmed with water can be kneaded and moulded. It is practically non-inflammable. It cannot be obtained perfectly transparent, nor in leaves thinner than 2 mm. in thickness. Galalith is protected by the German Patents, 115,681, 127,942, 141,309, and 147,994. Analogous products are produced in various ways by *Betz* (English Patent, 14,319, 1906), Desgeorge and Lebreil (English Patent, 23,789, 1906), *Goldsmith* (English Patent, 412, 1909), *Kathe* (English Patent, 17,953, 1907), *Schütze* (13,601, 1909). (See also English Patent, 21,750, 1910.)

A somewhat similar product is made by dissolving dried casein in dil. NaOH solution, heating with sulphur, evaporating the clear liquid to a syrup, and adding water-glass or zinc and lead hydroxides, and, to increase the hardness, emery, sand, cork dust, wood meal, etc. etc. The product is cast into plates and dried. See German Patents, 153,228, 163,818, and French Patents, 367,407.

Celluloid-like bodies are obtained by mixing nitrocellulose and casein; also by treating a compound of casein with a metallic oxide (German Patents, 138,783, 139,905).

(*c*) **Aldehyde-Phenol Condensation Products (Artificial Resins, Bone Substitutes, etc.).**—When certain aldehydes, such as formaldehyde and phenols, are boiled together, condensation occurs, and resinous bodies are formed, which can be used in the manufacture of varnishes, or plastic masses for imitating horn, ebonite, etc.

A remarkable product called **Bakelite**, after its inventor, Baekeland, is manufactured by warming together equal weights of phenol and formaldehyde, and a small amount of an alkaline condensing agent. The mixture separates into two layers, the upper an aqueous solution, and the lower an intermediate condensation product called A. If this intermediate product be heated above 100° C., a final condensation product called C is obtained in a porous, spongy state, which may be avoided by proceeding under a pressure of 50-100 lbs. per square inch. The product is then a hard, solid mass called **Bakelite**. Bakelite (sp. gr. 1.25) is very hard, not elastic, and an excellent insulator of heat and electricity. Its price is lower than hard rubber, casein, celluloid, etc.

Wood, *e.g.*, soft wood, may be soaked in the intermediate product A, and is then heated under pressure, whereby it becomes covered and impregnated with a brilliant coat of superior waxy varnish equal to the most expensive Japanese lacquer. With this coated soft wood results are obtained in making furniture which cannot be achieved even with the most expensive hard woods.

Cardboard, pulpboard, fibres, etc., when impregnated with A, on heating, produce a hard, polished material. It can be used for coating metallic surfaces; for replacing amber in pipe-stems; for buttons, billiard balls, knife handles, etc.; for compounding sawdust, wood pulp, emery, etc. etc. It is a very powerful cement, and can be used for making grindstones, bearings, etc.

A large number of condensation products of phenols and formaldehyde are producible, some of which are hard bodies, fusible, soluble in the usual solvents, forming substitutes for natural resins like shellac, etc., while others are hard, infusible, and insoluble substances, serving as substitutes for ebonite, celluloid, etc. Further information of these interesting products is given in *The Journal of Industrial and Engineering Chemistry*, vol. i. (1909), pp. 149, 545, *The Transactions of the American Electro-Chemical Society*, vol. xv. (1909), p. 597. (See also Patent Specifications (English), Nos. 1,921, 1,922, 2,122, and 21,566, A.D. 1908, and No. 8,875, A.D. 1905.)

The following notes on these interesting bodies will be useful. In 1871 Bayer showed that phenols and aldehyde react. Kleeberg in 1891, as the result of a violent action, obtained a hard irregular mass, insoluble and infusible, by allowing formaldehyde solution to act on phenol in the presence of HCl. Smith in 1899 moderated the violence of the action by solvents such as methyl or amyl alcohol; he also used acetaldehyde and paraldehyde, and finally evaporated, when a product was obtained which could be sawn, cut, and polished. Luft (1902) treats formaldehyde with phenol and acid in aqueous solution, and before the product has had time to harden he adds solvents such as glycerol, alcohol, or camphor. The product is similar to celluloid, but is less tough and flexible. Blumen (1902) adds an oxy-acid such as tartaric, and boils, thus producing a shellac substitute, which behaves like a soluble fusible natural resin. Fayolle in 1903 made a fusible **guttapercha substitute** by adding a large amount of glycerol to the H_2SO_4 used for condensing the product. Story (1908) added 3 parts of 40 per cent. formaldehyde to 5 parts of 95 per cent. cresol or carbolic acid, boiled eight to ten hours, concentrated, poured into moulds and dried *below* 100° C. The product was infusible and insoluble. Speyer (1897) condensed naphthol or polyphenols (*e.g.*, resorcin or pyrogallol) with excess of ammonia and formaldehyde, thus producing an antiseptic which slowly gives off formaldehyde. In 1907 F. Bayer & Co. produced a **shellac substitute** by using orthocresol. Grognot (1908) produced a shellac substitute in a similar manner, adding glycerol, and when the action is over distilling off the solvent. Helm in 1907 produced synthetic resins by using amines or ammonium salts as condensing agents.

(*d*) Horny substances (*i.e.*, those containing keratine), such as claws, hoofs, horns, hair, etc., when cut up, dissolved in alkalis, precipitated by acids, pressed and treated with formaldehyde, form hard products like celluloid. (See German Patent, 134,314.)

IX.—ARTIFICIAL SILK

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Several methods are now successfully worked for dissolving cellulose and squirting the solution through fine orifices, so as to form fine, silk-like threads. The founder of the industry was Chardonnet, who first produced "collodion silk."

(*a*) **Collodion Silk—The Cellulose Nitrate Process.**—Cellulose is treated with nitric acid, as in making gun-cotton, and thus converted into "collodion wool," a weakly nitrated cellulose, containing 10-11 per cent. of N, in the form of two nitro-groups, thus, $C_6H_8(NO_2)_2O_5$. Wood cellulose cannot be used for making the nitrocellulose, since it does not yield a stable enough nitro-product. Cotton cellulose, boiled with soda and bleached with chloride of lime, is now universally used. The nitrocellulose is dissolved in about 6 parts of a mixture of alcohol and ether (2 : 3) so as to form a thick syrup, which is carefully filtered and run into a tinned steel tank, where it is subjected to a pressure of about 50 atmospheres, and thus forced out in the form of very fine threads through a number of very fine glass tubes (*c*, Fig. 79), having openings of only 0.08 mm. diameter. According to the **wet process** the threads are spun out (squirted)—eight to thirty-six single threads simultaneously—into water, where they solidify and are continuously drawn off and twisted into a stouter single thread by a roller at *e*, Fig. 79. In the **dry process** of spinning (Chardonnet's original process) the threads are forced out into a warm air chamber, where the alcohol and ether instantly evaporate, and the solid threads are drawn off and spun together (twisted) to form stouter threads, just as in the wet process. The alcohol and ether vapours are condensed, and so the solvents are recovered.

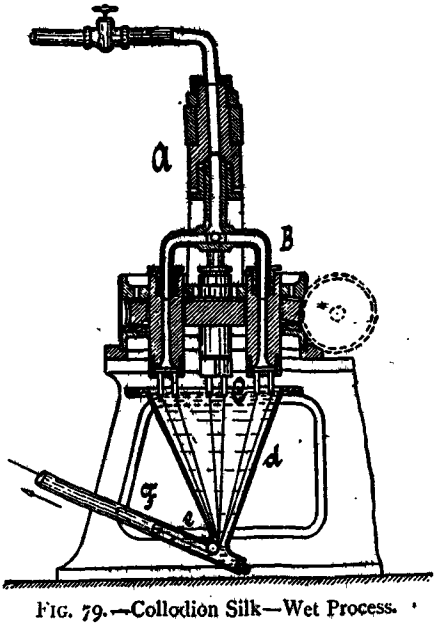

FIG. 79.—Collodion Silk—Wet Process.

Both the wet and dry processes of spinning have their own peculiar advantages and disadvantages. In the wet process (Lehner) a 10 per cent. collodion solution is used, and the process of spinning is somewhat slow. In the dry process (Chardonnet) a 20 per cent. collodion solution is used, and the process is rapid, but complex machinery is required to condense the vapours of alcohol and ether. At the present time the greater part of the artificial silk is obtained by one or other of these processes.

The threads so obtained are explosive and very inflammable. They are, therefore, passed through a reducing bath, which removes the nitro-groups and reconverts the substance into non-explosive cellulose. To prevent explosion it is extremely important that the threads should contain not less than a certain percentage of moisture until the denitration has been effected. The reducing bath usually consists of a 10 per cent. solution of sodium sulphohydrate ($H_2S + NaOH$ solution); sometimes calcium and magnesium sulphohydrates are also used. The nitrogen is reduced in a short time to 0.3 per cent., and the substance is now practically pure cellulose, being scarcely more inflammable than cotton. The denitrating process lessens the strength of the fibres, but increases their brilliance. The silk is well washed, bleached, washed, and dried.

The nitrocellulose process is a difficult and dangerous one. The nitrated cellulose is explosive, while alcohol and ether are very inflammable substances, giving vapours which seriously injure the health of the workmen. The chemicals used are expensive, and all the nitrogen used in the nitrating process is lost again in the denitrating process, and, indeed, up to the present is not recoverable. The great advantages of the process are: (1) the threads do not easily break in the winding and spinning process, so that there is little waste; (2) the collodion solution will keep indefinitely. In the other two processes to be described, the cellulose solutions are unstable and must be used soon after preparation. One of the great defects of the process has been the weakness of the threads after denitrating. Great improvements, however, have been effected in this direction. The gun-cotton product, however, is being slowly displaced by that prepared directly from cotton.

"Collodion silk" has been manufactured since 1891 in Chardonnet's large factory at Besançon. "Lehner silk" is a similar product manufactured in the Vereinigten Kunstseidefabriken in Frankfurt a. M. Enormous profits were made by some factories, and for a time the demand for the artificial brilliant silk was so great that its price actually rose for a time above that of real silk!

(*b*) **The Cuprammonium Process.**—This process depends upon the solubility of cellulose in a solution of copper hydroxide in ammonia.

The most important patents protecting the manufacture are those of *Pauly* (German Patent, 98,642, 1897); *Bronnert* (German Patent, 109,996, 1899); *Fremery and Urban* (German Patent, 111,313, 1899).

The cellulose is obtained from long-fibred cotton, purified by boiling with soda under 3 atmospheres pressure. The ammoniacal solution of copper is obtained (German Patent, 115,989) by charging an iron cylinder with copper turnings and adding a 20 per cent. ammonia solution and some NaOH solution (25° Bé.), while cold compressed air is driven into the solution. The temperature must not rise above 4° C. The solution should ultimately contain 45 g. of copper per litre, when it will take up 8 per cent. of cellulose. The solution must be as free as possible from inorganic salts. The percentage of cellulose dissolved increases with the percentage of copper present. The prepared cellulose is then mixed with the cuprammonium solution in special mixing or kneading machines, all contact with the air (and escape of ammoniacal fumes) being avoided. The solution is carefully filtered through fine metal cloth, so as to separate any undissolved fibres, and then forced through narrow orifices into a bath of sulphuric acid; the sulphuric acid removes the copper from the thread and gelatinises it; a 50 per cent. sulphuric acid is now used against a 10-20 per cent. formerly employed, as stronger threads of a higher lustre are obtained with the stronger acid. The individual threads are then spun together into thicker threads, consisting usually of eighteen single threads.

In order to remove completely all the copper, the threads are boiled with dilute acetic acid, washed with hot water, and dried on the spools (and therefore under tension) in a stream of warm air.

This variety of artificial silk is pure cellulose, and is sold under the names "Glanzstoff," "Sirius Silk," and "Meteor Silk." It is manufactured at Elberfeld (Vereinigte Glanzstofffabriken).

It is a strong product, possessing a very brilliant lustre, but with a somewhat feeble affinity for dyes.

(*c*) **The Viscose Process** (see also **Cellulose Solutions**, p. 188).—Cross and Bevan (English Patent, 8,700, 1892) dissolve cellulose by treating it with a concentrated solution of caustic soda, and then with carbon disulphide, as described on p. 189. The cellulose unites to form a water-soluble xanthogenate, NaS—CS—$OC_{12}H_{19}O_9$, known as viscose, thus :—

$$C_{12}H_{20}O_{10} + NaOH + CS_2 = CS\begin{matrix}SNa\\ OC_{12}H_{19}O_9\end{matrix} + H_2O.$$

The solution is prepared in a kind of hollander, and is carefully filtered through porous cellulose plates, from which it passes directly to the final spinning-orifices. These are situated in the bottom of a thick-walled, air-tight vessel, which is connected to an air-compression plant. The spinning-orifices consist of conical glass tubes (sometimes provided with platinum jets) with exceedingly fine orifices.

The viscid solution is then spun into a solution of ammonium chloride which separates out the cellulose again, and gives the product known as "viscose silk." Recently the spinning has been done in dil. H_2SO_4 containing alkali sulphate or organic substances. The threads must be washed free from sulphur by passing through a series of washing solutions. The cellulose xanthogenate is unstable, being rapidly decomposed by acids, more slowly by water or ammonium chloride solution, into cellulose and a sodium sulpho-carbonate. The cheap wood-sulphite-cellulose can be used in this process; it appears to be the one most likely to supersede the others, since it yields a product equal or superior in strength and softness, and is cheaper and simpler than the Chardonnet or Pauly process. For improvements see *Stearn*, German Patent, 108,511; English Patent, 5,730, 1904; American Patent of *Waite*, No. 816,404, 1906, (which displaces the dear ammonium chloride solution for spinning into by sodium bisulphite solution); German Patent, 187,947, and A. 296, C. 16,663.

Eschalier (German Patent, 197,965) treats the fibres with formaldehyde, and states that they are thus rendered strong enough for making clothes.

(*d*) **Silk from Cellulose Acetate.**—The artificial silk produced by the three preceding methods consists of a modified form of cellulose, akin to mercerised cellulose, which absorbs more water from the air than normal cellulose, thus producing a cellulose hydrate. Another variety of artificial silk is made, however, which differs from the preceding in being, not cellulose, but cellulose acetate. The triacetate $[C_6H_7(C_2H_3O_2)_3O_2]_n.H_2O$ is often used, but other acetates are employed as well. For preparation and properties see under **Cellulose Esters.**

Cellulose acetate forms a horny mass, which dissolves in chloroform, glacial acetic acid, ethyl benzoate, and nitrobenzene, to form a thick, syrup-like solution, which may be squirted through holes into alcohol or ammonium chloride, so as to form fine, silk-like threads. Such "acetate silk" is considerably stronger and harder than cellulose artificial silk, and is non inflammable, but has the disadvantage of being much dearer.

"**Acetate silk**" is an even better non-conductor of electricity than rubber or natural silk. An important commercial application is the coating of very fine copper wire for electrical purposes.

Formates of cellulose have also been proposed for making artificial silk (see p. 216).

(*e*) Other Varieties of Artificial Silk

Vandura or Gelatine Silk, a very beautiful product, made from gelatine and formaldehyde, and having about the same percentage of nitrogen as natural silk, is too weak to be of much practical use. (See German Patent, 83,225.) Gelatinous silks, made from gelatine from sea-weed, Irish moss, agar-agar, etc. etc., have been proposed. (German Patent, 148,587.)

Casein Silk.—Casein dissolved in alkali or zinc chloride solution is forced into acid or other precipitating and hardening bath. (See German Patents, 170,051, Supp., 178,985, 182,574.) These

products up to the time of writing have attained little importance, but may ultimately do so when improved.

(*f*) Coarse Artificial Fibres for Various Purposes

Artificial Hair has long been made by *Lehner* by the collodion process (which see, p. 212), by spinning out simultaneously several fine threads in such a manner that they meet while still in a soft condition, and then coalesce to a single thread of suitable dimensions. (See German Patent, 125,309.) The product is known as **Meteor Yarn** and **Sirius Yarn**, etc., used for cording in millinery. (Stout single threads squirted out from a large orifice of the proper dimensions are too weak to be of much use.) Instead of coalescing a number of fine threads, the German Patents, 129,420, 181,784, 186,766, and American Patent, 856,857, pass cellulose threads through solvents, which soften and partially dissolve the individual fibres of the thread, making them cohere together to a single homogeneous thick fibre, with a polished and smooth surface. The thread is then hardened.

If the artificial hair is to be used for making wigs, the lustre must be removed by various processes. (German Patents, 129,420 and 137,461.)

Artificial Hemp Bast may be prepared by mixing in zinc white, barium sulphate, chalk, etc., into a collodion, viscose, or other solution of cellulose, and then steeping fibres in the solution. (German Patent, 184,510.)

Properties of Artificial Silk.—Artificial silk possesses a more brilliant lustre than natural silk, and dyes well with cotton dyes, collodion silk even directly taking basic dyes. Artificial silk, however, has a much harsher feel than that of real silk; this is in consequence of the greater thickness of the threads, thus while real silk has a thickness of only 0.01-0.02 mm., the finest threads of artificial silk barely reach 0.03 mm. The reason of this is that up to the present it has been found impossible to make the openings in the glass spinning-tubes of a smaller diameter than 0.08 mm., although no doubt this difficulty will be overcome in time.

A more serious defect, however, is the want of strength, especially in a wet condition. In a dry condition the strength equals that of heavily weighted natural silk. The strength has been increased considerably of recent years, a toughening effect being produced by soaking in formaldehyde and similar chemicals (*e.g.*, see German Patents, 197,965, A. 296, C. 16,663). It has been found that the finer the fibres the stronger the woven cloth, and efforts have, especially in recent years, been made to spin finer and finer threads; on these lines the strength of natural silk may ultimately be attained or even exceeded.

Uses of Artificial Silk.—Artificial silk is used in rapidly increasing quantities for glittering braids and trimmings, and for relief on cotton cloths. Indeed for these purposes it is far better than real silk, since it gives excessive brightness to the fabric. It is also used in the form of **insertions** for ladies' blouses, ties, scarfs, and wearing apparel generally. Furniture stuffs and carpets are now beginning to be manufactured from it. Such artificial silk cloth is much more readily freed from dust than real silk cloth. Artificial silk, however, being much weaker than real silk (at least most of the kinds in use up to the present), is unsuitable for using in a pure state for making cloth. It is invariably used with other strong threads as backing.

This explains why the manufacture of artificial silk has not to any extent affected the volume of the trade in real silk, since it is used for a different purpose. About 25,000 tons of real silk are annually produced, while the output of artificial silk amounts from 5,000-7,000 tons yearly (1910). The English output was 270 tons in 1909. 1 kg. of artificial silk costs 15s. to 20s.; of real silk, 20s. to 40s. The introduction of artificial silk, however, in large amounts has had the effect of considerably lowering the prices paid for real silk, and should an artificial silk be ultimately produced having the mechanical strength and wearing properties of real silk, it may in time entirely displace it.

The English export of **artificial silk** amounted to £196,000 in 1910. The import amounted to £36,000. The United States imported 1,542,000 lbs. (value $2,062,000) in 1910.

Artificial silk is also used for making artificial horse hair, hair for wigs, etc. Also for making incandescent lighting mantles, which are said to be very elastic and durable, with a longer and greater incandescent power than other kinds.

Tests of Artificial Silk Yarns.—Natural silk contains 17 per cent. of nitrogen. The various artificial silks contain from 0.07-0.16 per cent. N.

Diphenylamine Sulphate gives the following reactions:—

Silk	Brown coloration.
Tussah silk	,, intense.
Chardonnet and Lehner (nitrocellulose)	Intense blue.
Pauly, Viscose, or Yarmouth silks	No reaction.

A good method of distinguishing artificial silk from real silk or mercerised cotton is to heat the cloth to be tested for ten minutes to 200° C. Artificial silk is carbonised (though intact as regards structure) and falls to pieces on touching or rubbing, while real silk, cotton, or wool are hardly affected. Hence rubbing the heated and cooled cloth removes the artificial silk as dust, and by comparison with a piece of the original cloth the number of threads of artificial silk can be easily counted. Under the polarisation microscope dyed natural silk does not appear dichroic, while dyed artificial silks (of cellulose) are strongly dichroic if dyed with methylene blue, congo-red, or benzo-azurine (Herzog).

Cellulose Esters

Literature. W. Massot.—"Faser- u. Spinnstoffe." *Z. Angew. Chem.*, 1912, 567.

Cellulose Acetates.—Several of these appear to exist, but according to Ost (*Zeit. f. Angew. Chem.*, 1906, S. 993) even the highly acetylated products, the so-called "Tetra-acetates," are really Triacetylcelluloses, $[C_6H_7(C_2H_3O)_3O_5]_x.H_2O$ (disputed).

Lederer produces the triacetate by first treating cellulose with dilute acids, thereby converting it into hydrocellulose, and then acetylating with acetic anhydride and a very little concentrated H_2SO_4 or glacial acetic acid, the process being carried out in the cold. (See English Patents, 11,749, 1900; 7,088 and 11,164, 1902; 734, 1903; 7,346 and 19,107, 1906; 3,103, 1907.) Another process directly acetylates the cellulose, which at the same time undergoes partial hydrolysis (Ost).

Cellulose acetate is also made on the industrial scale from cellulose regenerated from the sulpho-carbonate or viscose. Henckel-Donnersmonk's process consists in heating molecular proportions of cellulose and magnesium acetate with acetyl chloride, anhydrous acetic acid, and nitro-benzene.

It is soluble in chloroform, ethyl-benzoate, glacial acetic acid, and nitro-benzene, and is insoluble in methyl or ethyl alcohol, ethyl or amyl acetate, acetone, and ether.

It forms films of great transparency, is a better electric insulator than rubber or silk, and is non-inflammable. An important commercial application is the manufacture of "acetate" silk for coating very fine copper wire for electrical purposes (p. 214). Its price in 1910 was about thrice that of nitrocellulose.

Non-inflammable celluloid substitutes are made by mixing the less highly acetylated cellulose acetates with camphor. The so-called "**Cellite**" films for kinematographs are made in this way, and are only with difficulty inflammable. Combs, toys, balls, etc., of this "**cellite**" are now manufactured and used as a substitute for the highly inflammable and dangerous celluloid. See under **Celluloid.**

Cellulose Formates are made by acting on the cellulose with first sulphuric acid and then formic acid. A mixture of formates ensues which can be used for making artificial silk. (See English Patent, 17,936, 1909.) For an account of **other cellulose esters** see Piest, "Die Zellulose," Stuttgart, 1910.

For esters of HNO_3 see **Gun-cotton** (pp. 624-629) and **Collodion**, p. 207.

SECTION V

Fermentation Industries

FERMENTATION INDUSTRIES

I.—FERMENTS, ENZYMES, BACTERIA, MOULDS, YEAST, ETC.

BY G. MARTIN, Ph.D., M.Sc.

Nature of Fermentation.—Fermentation is the decomposition of complex organic material into substances of simpler composition by the agency either of protoplasm itself, or a secretion prepared by it (Green). Those agents which bring about fermentation are called "ferments."

Most of the countless chemical changes which occur in the animal and vegetable kingdom—some of them of a truly wonderful nature—may be traced to the action of "ferments." Such changes include processes of oxidation and reduction, putrefaction of organic matter, formation and splitting up of fats, ester formation, production of alcohol from sugar, etc. etc.

Many of the oldest industries in the world's history—the making of wine, beer, and vinegar, the souring and clotting of milk to form cheese, the tanning of hides—are dependent upon the action of ferments to which bacteria and other organisms or living tissues give rise. The same is also true of the fermentation processes employed in the extraction of natural indigo, in the preparation of coffee and cocoa, in the curing of tea and tobacco, and in the retting of flax.

So far as technical chemistry is concerned, the most important "ferments" are those which cause the generation of alcohol from sugar and starch, and to which we owe the enormous alcoholic industries of to-day. Before giving particulars of alcoholic fermentation, we deem it advisable to give a brief survey of the other ferments, referring the reader for further information to the very numerous standard works on the subject, a list of which is given below.

For our purpose "ferments" may be divided into two classes:—

A. **Unorganised Ferments or Enzymes.**
B. **Organised Ferments.**

A. THE ENZYMES OR UNORGANISED FERMENTS

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HARDEN AND YOUNG.—"The Alcoholic Ferment of Yeast-Juice," *Roy. Soc. Proc.*, B., 77 (1906), 405; 78 (1906), 369; 80 (1908), 299; 81 (1909), 336.
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Enzymes are complex nitrogenous substances of exceedingly high molecular weight and similar in elementary composition to the albuminous substances. They are soluble in cold water, forming very slightly diffusible solutions, from which they may be precipitated by alcohol or ammonium sulphate as a white amorphous powder. In solution their chemical activities are weakened at 60° C., while a temperature of 80° C. usually destroys them. When dried, however, they will often stand considerably higher temperatures. Their aqueous solutions rapidly

putrefy. In glycerol, however (in which they are soluble), they may be preserved for a considerable time. Antiseptics and strong mineral poisons, such as formaldehyde, phenol, strong mineral acids or bases, lead, copper, mercury or zinc salts, potassium cyanide, etc., destroy enzymes. Enzymes possess the remarkable property of attacking complex organic molecules, splitting them up or "hydrolysing" them into simpler substances, usually with the addition of water. They thus render soluble substances like starch, fats, albumen, etc.

A similar hydrolysing action is caused by mineral acids or bases, or superheated water, and, according to Professor W. Ostwald, the enzymes merely accelerate actions which could occur, although slowly, under normal conditions even without the presence of an enzyme. The enzymes are thus regarded as "contact substances," as they themselves undergo but little change, a very small quantity of an enzyme being capable of hydrolysing enormous quantities of material. In certain cases ferments can also effect a synthetic process. Thus Croft Hill has been able to produce isomaltose by the action of the enzyme maltase upon dextrose: $2C_6H_{12}O_6 = C_{12}H_{22}O_{11} + H_2O$. Emil Fischer and his co-workers have synthesised certain decomposition products of albumen by means of enzyme action, while Kastel and Loevenhart have synthesised ethyl butyrate by bringing together ethyl alcohol and butyric acid in the presence of the fat-splitting enzyme lipase. The researches of Croft Hill, Kastel and Loevenhart, etc., show that enzyme action is in many cases *reversible*.

The enzymes are very widely distributed in the living world, both animal and vegetable, occurring in the saliva, in the gastric juices, in the pancreas, kidneys, blood serum, and plant juices. By their aid the foodstuffs are rendered soluble and digested. The enzymes are produced directly by *living* protoplasm cells from albumen and similar substances; once formed they may, as stated above, be removed from the plant or animal, and retain their activity for a considerable time.

Each enzyme is characterised by its capacity of performing **one specific chemical action**, and they are most easily classified according to the actions they perform.* Thus we have:—

1. **Diastatic Enzymes**, which dissolve insoluble carbohydrates like starch and cellulose, converting them into soluble sugars.

The best known and most important vegetable enzyme is **amylase (diastase)**, which occurs in **malt** (germinating barley) and other germinating seeds, and in many fungi. It occurs only in traces in the raw corn grain itself, but develops rapidly when the grain begins to germinate.

It may be obtained by extracting green malt with cold water, and precipitating with alcohol or ammonium sulphate. It then forms an amorphous powder which is purified by repeatedly re-dissolving and reprecipitating, and by subjecting to dialyses. The product thus obtained possesses a varying composition, those preparations being most active in which the elementary composition (especially the nitrogen) approximates most closely to albumen. Thus we may get

C	44-52 per cent.	S	1-2 per cent.
H	7-6.6 ,,	O	33-23 ,,
N	9-16 ,,	Ash	5-6 ,,

Vegetable diastase rapidly dissolves starch, producing **maltose**; the optimum temperature is 40°-60° C.; at 80° C. it becomes inactive and coagulates. In a dry condition it can stand a temperature of 150° C., becoming inactive at 158° (Hueppe).

Ordinary **vegetable diastase** is undoubtedly a mixture of several distinct enzymes. One of these hydrolyses the starch to **dextrines**, and then stops its action. Another hydrolyses the **dextrines** to **maltose**.

It should be noted that ordinary malt contains in addition to diastase also ferments like **glucase** (maltase), **invertase**, and **proteolytic ferments** (see below).

Saliva diastase (ptyalin) in saliva and **pancreas diastase** (amylopsin) behave similarly to vegetable diastase, but are apparently not identical with it. **Inulase** decomposes inulin; **cytase** or **cellulase** dissolves cellulose, destroying cell-walls and thus allowing diastase to attack the enclosed starch.

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* The nomenclature now generally adopted is to denote each enzyme by the name of the substance it especially attacks, with the addition of the suffix "ase," *e.g.*, **maltase** is the enzyme which decomposes maltose, **cellulase** that which decomposes cellulose.

2. **Inverting Enzymes.**—These transform sugars of the biose type (disaccharides) into simpler sugars, usually hexoses.

Invertase or **Sucrase** hydrolyses cane-sugar into *d*-glucose and *d*-fructose; most rapidly at 55°-60° C. It is inactive at 75° C. It is contained in yeast cells, and may be obtained from them by drying at 105° C., extracting with water, and precipitating with alcohol; also contained in malt. Easily soluble in water and diffusible, and acts only in acid solution. May be heated when dry for one hour at 140°-150° C.

Maltase or **Glucase** converts maltose into 2 molecules of glucose; occurs in malt and in many culture yeasts. Is difficultly soluble in water and can only be extracted from crushed and ground cells by leeching. Optimum temperature, 40° C. Destroyed at 50°-55° C.

Lactase converts milk sugar (lactose) into *d*-glucose and *d*-galactose; occurs in milk sugar yeasts (S. Kefir) and some culture yeasts, never in brewing culture yeast. Does not diffuse or penetrate the cell wall.

Melibiase, which is present in some bottom-fermentation yeasts and absent from most top-fermentation yeasts, splits **melibiose** into *d*-glucose and *d*-galactose. Obtained by leeching dried cells with water; cell diffusible.

Trehalase splits trehalose, not diffusing.

3. **Ferments which decompose Glucosides.**—**Emulsin**, contained in bitter almonds, decomposes the glucoside amygdalin into grape sugar, benzaldehyde, and hydrocyanic acid. **Myrosinase**, the ferment of **black mustard seed**.

4. **Proteolytic Enzymes.**—These decompose the various soluble and insoluble proteid substances (such as albumen, fibrin, etc.) into simpler bodies, such as peptone, etc., sometimes decomposing them into simple amido-acids, such as leucin, tyrosin, aspartic acid, etc.

Among these enzymes we may mention the **pepsin** of the mucous membrane of the stomach, which decomposes albuminous bodies into **peptones**, and is most active in the presence of 0.02-0.04 per cent. free HCl; **trypsin**, the proteolytic ferment of the **pancreas**, which decomposes albuminous substances into leucin, tyrosin, and other amido-acids; **papain**, of the papaw tree, acts on flesh.

Yeast Endotryptase.—Optimum action occurs in 0.2 per cent. of HCl; optimum temperature, 40°-45° C., destroyed at 60° C.; retains efficiency in yeast juice nine to fifteen days at 37° C., and converts yeast albumen into tyrosin, leucin, xanthine bodies, and passive albumoses, but not into peptones.

5. **Clotting Enzymes**, *e.g.*, **rennet (lab, chymosin)**, which coagulates milk precipitating the casein, but leaving the milk sugar in solution. Prepared from stomach of calf by macerating with water. Also occurs in **yeast cells**. Destroyed at 65° C. (two hours); non-diasable. **Thrombase**, which coagulates blood; **pectase**, which produces vegetable jellies.

6. **The Lipases**, which split up fats into glycerin and fatty acids. Occurs in the **pancreas**, also in various seeds, especially in castor seed. (See p. 93.)

7. **Oxidases**, which oxidise various substances, *e.g.*, **laccase**, **tyrosinase**. **Oxydase** and **cutalase** occur in yeast cells.

8. **Enzymes**, which decompose **amides**, *e.g.*, **urase** in urine, which splits up urea into CO_2 and NH_3.

9. **Alcohol Producing Enzymes**, *e.g.*, Buchner's **zymase**, secreted by yeast cells, which decomposes grape sugar, etc., directly into alcohol and CO_2.

Zymase will not pass through the yeast-cell wall and hence can only be isolated by breaking down the cell wall. This Büchner effected in 1897 by grinding up the living yeast cells with quartz sand and kieselguhr (infusorial earth) and then pressing out the juice in a filter press under a pressure of 400-500 atmospheres. The clear opalescent fluid rapidly ferments cane sugar, grape sugar, and fructose, but not lactose or mannitol. The action is not stopped by chloroform nor by passage

of the liquid through a Berkefeld filter, or dialysing membrane. The fermentation is a true alcoholic one, in that alcohol and CO_2 are produced in the same proportion as when living yeast is used. The same by-products—such as glycerol and succinic acid—are also produced.

Zymase may be precipitated by alcohol-ether or acetone from its aqueous solution, and after drying is obtained as a white amorphous powder, which (even after prolonged keeping) when redissolved in water does not lose its fermentative power.

It does not appear to be sensitive to the action of dry heat up to 100° C., since yeast thus killed still contains the active ferment. Büchner's expressed yeast juice rapidly loses its alcohol-producing power on standing, the zymase being destroyed by another enzyme, which is capable of digesting albumen, namely, a proteolytic enzyme called **endotryptase**, which also causes the auto-digestion of yeast cells. The destruction occurs most rapidly at 40°-50° C.

R. Albert prepares his **zymin** or **permanent yeast** (*Dauerhefe*) by partially drying ordinary yeast, immersing in ten times its volume of acetone for fifteen minutes (which kills the living yeast), drying on filter paper, and well washing with ether, finally drying at 45° C. The white powder so obtained contains only **dead yeast** cells (with cell walls intact), and contains the **zymase ferment** uninjured. Consequently it will bring about vigorous fermentation, even after keeping for years.

Albert's process is interesting because yeast cells which have died in the ordinary way will not yield a juice capable of fermenting sugar. This only occurs when the cells are killed by acetone or alcohol (as above described), which at the same time acts as a preservative on the zymase ferment in the cell. It should be noticed that zymase certainly consists of several enzymes. Harden and Young have shown that when Büchner's yeast juice is forced through a Martin filter it is separated into two parts, namely, a residue (colloidal and non-diasable), which remains behind, and a liquid, which passes through the filter. Neither this residue nor the liquid which passes through are separately capable of causing alcoholic fermentation. On mixing them, however, a vigorous alcoholic fermentation is produced. Hence the alcoholic fermentation is due (1) to a colloidal, (2) to a crystalloidal substance.

Harden and Young have shown that phosphoric acid is one necessary constituent of the dialysable (crystalloidal) substance taking part in the fermentative action. For every molecule of sugar which is broken down into alcohol and CO_2, a molecule of a comp'ex hexose phosphate (a compound of a sugar molecule with two of phosphate) is simultaneously formed, and this phosphate passes repeatedly through the cycle of changes represented in the following equations:—

$$(1)\quad 2C_6H_{12}O_6 + 2K_2HPO_4 = 2CO_2 + 2C_2H_5OH + 2H_2O + C_6H_{10}O_4(PO_4K_2)_2.$$

$$(2)\quad C_6H_{10}O_4(PO_4K_2)_2 + 2H_2O = C_6H_{12}O_6 + 2K_2HPO_4.$$

The rate of fermentation by yeast cells and the factors governing it have been exhaustively studied by Arthur Slator and H. J. S. Sand, see p. 239.

B. ORGANISED FERMENTS

LITERATURE

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The chemical changes involved in the processes of alcoholic fermentation and in the putrefaction and decay of organic matter are due to the presence of minute organisms, which for convenience we group under the name "organised ferments."

It was once thought that these chemical changes were brought about by the direct action of the living protoplasm of these organisms. It is now, however, almost universally believed that these minute organisms *secrete* enzymes, which by their "contact" action bring about the various changes, and consequently that all such changes in reality are a direct consequence of unorganised ferments or enzymes.

The micro-organisms whose chemical activities are thus grouped under the general name of "Fermentation" are minute chlorophyll-free **plants**, belonging to the great family of "**Fungi**." So far as the fermentation industries are concerned, they may be divided into three groups: (1) **Bacteria**, (2) **Moulds**, (3) **Yeasts**.

Bacteria (Schizomycetes)

Bacteria are the lowest forms of vegetable life, and the smallest living organisms that we are acquainted with, often requiring a magnification of over 300 diameters before becoming visible. They multiply either by splitting into two (*i.e.* by **fission** or cell-division—hence their classification among the fission-fungi and their name **schizomycetes**) or by **spore-formation**, *i.e.*, by the production of small protuberances, which eventually separate from the main organisation. These spores are often extraordinarily resistant towards heat, cold, want of nutrition, and even poisons. They germinate under favourable conditions into organisms similar to the parent organisms. Bacteria are colourless (devoid of chlorophyll) plants and possess an envelope or capsule consisting of cellulose or allied substances. They are monocellular organisms, existing as—

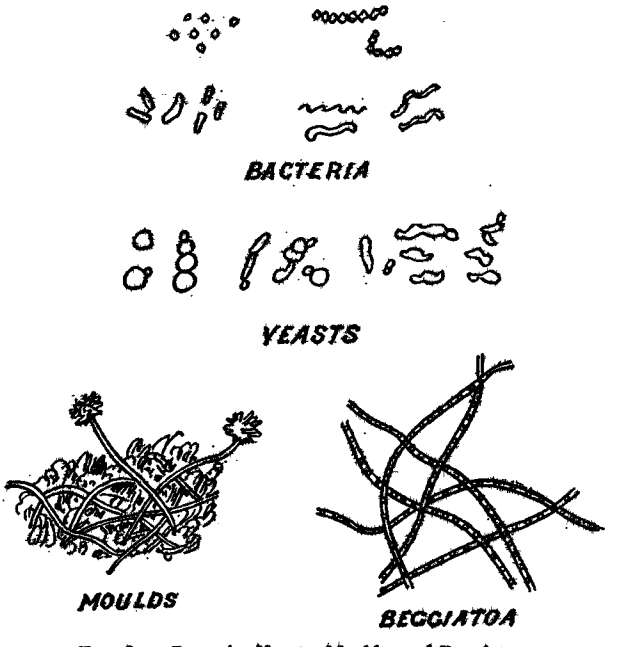


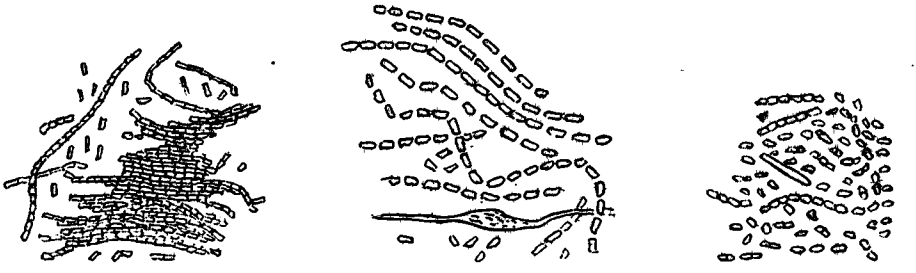
FIG. 80.—Bacteria, Yeasts, Moulds, and Beggiatoa.

1. Round cells (coccaceæ), often less than 0.001 mm. diameter.
2. Rods (bacteriaceæ), sometimes united into long **threads**.
3. Leptotricheæ } higher bacteria.
4. Cladotricheæ }

They are often provided with delicate threads—**flagella** or cilia—which serve as locomotive organs.

Bacteria are very widely distributed in nature. In unnumbered millions they occur in the air, soil, and water. On account of their minuteness they are rapidly transported by the wind and blowing dust from place to place. Wherever food is plentiful they develop enormously, and thus it is that all dead plants and animals are rapidly consumed by them, undergoing, as the result of bacterial vital activity, the familiar phenomena of putrefaction and decay. Their most important function is the breaking down of complex organic substances into simple inorganic compounds, which are again available for plant nutrition.

Certain bacteria produce strong poisons as the result of their vital activity. For example, the **ptomaines**, or alkaloids of decay, which are found in putrefying flesh. Others are capable of producing chemical changes in the bodies of higher living organisms, and in the case of specific diseases—(caused by "pathogenic" bacteria), such as cholera, typhus, diphtheria, etc.—generate poisons (toxins), which are the direct cause of the illness. Artificial cultures of these bacteria also produce those poisons which, if injected into an animal, set up the same symptoms of disease as if produced by the multiplication of the microbes within the animal. To defend themselves against such bacterial poisons, animals produce in their serum antidotal poisons known as "anti-toxins"—which are probably enzymes—and use is made in Medicine of this fact in the curative treatment of



Bacterium Aceti. *Bacterium Pasteurianum.* *Bacterium Kützingianum.*

FIG. 81.—Acetic Acid Bacteria (Hansen).

disease. Thus the Farbwerke Höchst manufacture an anti-toxin from the serum of horse blood, which when injected into a patient cures diphtheria. Similar inoculating serums are used in the treatment of plague and other diseases. Bacteria require as food certain mineral and organic material. Many require oxygen, while some are killed by it ("anærobic bacteria"), others can develop both in the presence and in the absence of oxygen. There are innumerable races of bacteria—quite as definite in character as animals or plants—and pure cultures of the individual races are made by methods in vogue in bacteriological technique, for an account of which the reader is referred to one of the special text-books dealing with the subject. See also **Yeast**.

Most bacteria are destroyed by antiseptics. They are also usually killed by steam at 100° C.; they are almost instantaneously killed by high-pressure steam.

The following varieties of bacteria are of great use in the chemical industry:—

FIG. 82.—Lactic Acid Bacteria in Sour Milk. (*Bacillus Bulgaricus.*)

Acetic Acid Bacteria.—These cause the oxidation of alcohol into acetic acid, thus: $CH_3.CH_2OH + 2O = CH_3.COOH + H_2O$. Several varieties exist, such as *Bacterium aceti*, *Bacterium Pasteurianum*, *Bacterium Kützingianum*, and *Bacterium xylinum*, etc. They grow in dilute alcoholic fluids (containing under 10 per cent. alcohol), such as wine and beer, which contain the mineral and nitrogenous matter necessary for their nutrition. Continental varieties develop best at 30°-35° C., and require oxygen. According to Mitchell (see **Vinegar**) English varieties flourish at 40°-43° C. As the result of their activity, a thick skin—known as the **vinegar plant**, or "mother of vinegar"—covers the surface of the fermenting liquid, sometimes to the depth of 1 in. It is formed of the extensively developed mucinous envelope of the cells, and consists principally of cellulose. The bacteria occur as short rods, 0.001-0.003 mm. in length, often attached together in chains by their mucinous envelope. They occur widely distributed in fermenting liquids wherever there is plenty of air. They are used technically for the manufacture of vinegar (which see, p. 315).

Lactic Acid Bacteria.—These split up sugar into lactic acid, thus: $C_6H_{12}O_6 = 2C_2H_4(OH).COOH$, and are the cause of the souring of milk. Their optimum temperature is 30°-50° C., and being capable of developing at 50° C.—a temperature unfavourable for most other organisms—can easily be obtained as pure cultures. They occur on fruit, corn grains, malt, etc., and are cultivated extensively for the manufacture of **Lactic Acid** (which see, p. 317).

Butyric Acid Bacteria ferments lactic acid (and, it is stated, sugar and other carbohydrates) directly into normal butyric acid, the change being accompanied by the evolution of CO_2 and H, thus: $2C_3H_6O_3 = C_3H_7.COOH + 2CO_2 + 2H_2$.

Many varieties of these bacteria exist, occurring on fruit, and causing the souring of cut beet, spent malt, distillers' wash, etc., the ripening of cheese, the rotting of wet potatoes, and the retting of flax. Certain kinds (*e.g.*, *B. amylobacter*) dissolve cellulose. In the brewing industries the presence of butyric acid bacteria may cause great damage. The best known variety is the *Bacillus butyricus*, which consists of thin, motile rods, having an optimum temperature of 40° C., and flourishing in the absence of oxygen. (See **Butyric Acid**, p. 320.)

Proteolytic Bacteria are used in the tannery in the "bating" or "puering" process. These bacteria produce digestive enzymes which have a solvent action on the fibres of the skin, rendering it more supple. They have been studied and described by Mr J. T. Wood (see *Journ. Soc. Chem. Ind.*, 1910, 29, 666), who has successfully made use of a puer-substitute called "erodin" which consists of a culture medium of peptonised gelatinous tissue, with a special mixed culture of selected bacteria (see pp. 580, 581).

Nitrogen-fixing Bacteria.—A number of bacteria exist in the soil, which cause the gradual fixation of atmospheric nitrogen, the oxidation of ammonia to nitrites, and of nitrites to nitrates. They are of the greatest importance to agriculturists. Two well-defined organisms convert **ammonia** into nitrites, viz., **nitrosomonas** and **nitrosococcus**. The **nitric** organism, which oxidises the nitrites to nitrates, is a very small bacterium.

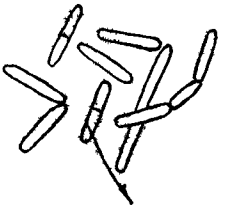


FIG. 83.—Butyric Acid Bacteria.

Other bacteria are used technically in the dairy, in the preparation of indigo, tobacco, tea, etc., and especially in the modern method of sewage disposal, where the noxious substances are completely oxidised to CO_2, water, etc., by special bacteria cultivated in the filter beds. **Sulphur** bacteria exist which absorb H_2S and other sulphur-containing compounds, oxidising them to sulphates. A. Fernbach (pp. 314, 333) has produced cultures which give *fusel oils* (butyl alcohol) and *acetone*.

Moulds (Hyphomycetes).

These are more highly organised than bacteria or yeasts; they propagate from **spores** (conidia), which develop into long threads of cylindrical cells forming a network known as **mycelia**. From these cells special seed-bearing organs—the **hyphæ** or **thalli**—develop. The moulds derive their names from these organs.

Moulds readily develop in sugar solutions, on moist bread, fruit, moist corn grains, wood, and even on damp walls. They act both as oxidising and hydrolysing ferments, and are, as a rule, not harmful.

Among the more widely distributed moulds may be mentioned: *Penicillium glaucum*, a green mould; *Aspergillus glaucus*, likewise green; *Aspergillus niger*, which appears dark. All these oxidise **sugar**, generating organic acids. They also contain enzymes, which hydrolyse **starch** and albumen. Two kinds of moulds—*Citro-myces*—are known which oxidise sugar (up to 50 per cent.) into **citric acid** in the presence of $CaCO_3$, and have been used technically for that purpose, but up to the present without success (see **Citric Acid**, p. 374).

Two moulds, *Aspergillus Oryzæ* (Japan) and *Mucor* (*amylomyces*) *Rouxii* (China), grow on rice, and are used for making **saké** (rice beer) and **arrak** from rice (in the same way that we use **malt** for making beer from corn grains), since they contain **diastase** (or a similar enzyme), which hydro-

lyses rice starch into **fermentable sugars**. They have been employed for this purpose in Europe (see **Amylo Process**, pp. 286, 249). The mould *Mucor racemosus* splits sugar into alcohol and CO_2.

Yeasts (Saccharomycetes)

The yeasts are single-cell fungi, more highly developed than bacteria, but less developed than moulds. They propagate by the formation of small daughter cells or buds, which are extruded from the parent cell—hence their name "budding fungi." Some yeast fungi have been observed to propagate by fission. Many species form endospores under special conditions, while other species do not possess this capacity. Yeasts will only develop in media containing sufficient nitrogenous and mineral food for their nutrition.

Alcoholic Fermentation.—Yeast fungi decompose sugar into alcohol and carbon dioxide, according to the equation: $C_6H_{12}O_6 = 2C_2H_5.OH + 2CO_2$. The monosaccharides (hexoses)—dextrose, laevulose, mannose, galactose—are thus decomposed by all true yeasts. The disaccharides—cane sugar and maltose—are not directly fermented in this manner, but have first to be hydrolysed into monosaccharides by enzymes contained in the yeast. **Milk sugar** is only fermented by a few yeasts which contain the enzyme **lactase**. Most yeasts do not contain

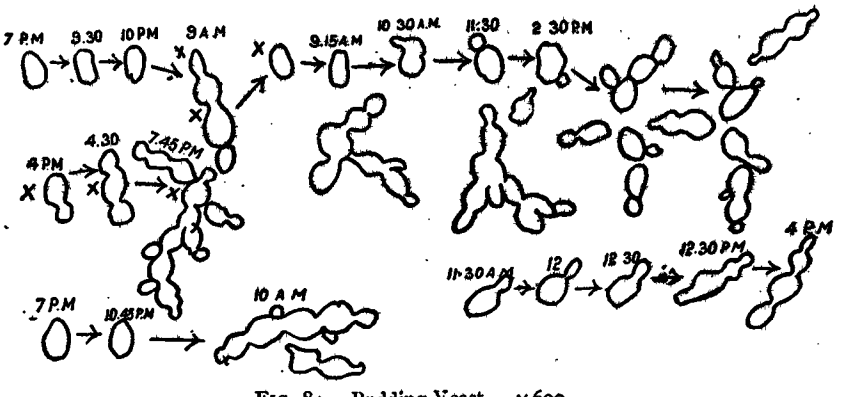


FIG. 84.—Budding Yeast. ×600.

enzymes which hydrolise **starch** and **cellulose**, and hence these substances have to be converted into sugars by **diastase** (*e.g.*, in malt) before yeasts can ferment them into alcohol. See p. 239 for **Rate of Alcoholic Fermentation.**

Only about 95 per cent. of sugar is transformed by alcoholic fermentation into CO_2 and alcohol, for about 5 per cent. of by-products—such as glycerol, succinic acid, fusel oils, and higher alcohols—are produced as the result of the vital activity of the yeast cells. Thus, according to Pasteur, 100 parts of glucose yield on fermentation :—

Alcohol	48.4
CO_2	46.6
Glycerol	3·3
Succinic acid	0.6
Fusel oils and cellulose	1.1
	100.0

It is traces of these by-products which give a characteristic taste and smell to different alcoholic liquors. From grape juice (must) we get the scenty "wine oils" which give a "bouquet" to the wine. Potato starch yields unpleasant smelling "fusel oils." See pp. 251, 298, 314.

A. Fernbach has obtained cultures which produce *fusel oils* and *acetone* (see pp. 314, 333).

Enzymes contained in Yeast (see p. 221).—The yeast cell is surrounded by a thin wall of cellulose and pectose. The living protoplasm enclosed within this wall secretes several enzymes, some of which are capable of diffusing through the

wall (and hence may be extracted by water or solvents), while others cannot do so, and can only be obtained by rupturing the cell walls and extracting. Such enzymes are called "intracellular" or "endo-enzymes," and obviously can only exert a chemical action on substances capable of diffusing through the cell wall into the living protoplasm.

The following enzymes occur in yeast (after Emil Schlighting) :—

1. **Hydrolysing Enzymes**:—

   (*a*) **Sugar Splitting.**—Invertase, maltase, lactase, melibiase, raffinase, trehalase, diastase, and a glycogen-splitting yeast which plays an important part in **self-fermentation** or **auto-digestion** of the yeast cells. These enzymes have been treated on p. 221.

   (*b*) **Proteolytic.**—Endotryptase. Plays an important part in auto-digestion of yeast cells. For properties, see p. 221.

   (*c*) **Coagulating.**—Rennet, obtained by extracting yeast cells with $CHCl_3$ under pressure at 60° C.

2. **Oxidising.**—Oxydase, catalase. Destroyed at 60-65° C.

3. **Reducing Enzymes.**—Optimum temperature, 40° C.

4. **Alcohol-producing Enzymes—Zymase.**—This directly splits up sugar into alcohol and CO_2, and is the cause of the alcoholic fermentation produced by yeast. Described p. 221.

Chemical Composition of Yeast.—The following analyses are typical of ash-free dry yeast substances (different samples vary) :—

	C	H	N
Top Yeast	48.6	6.8	11.5
Bottom Yeast	45.0	6.7	8.7

Old yeast is poorer in N. Moisture, 75-83 per cent.; S, 0.39-0.7 per cent.

Yeast Ash varies from 2.5-11.5 per cent., and consists, approximately, of :—

$KH_2PO_4 + K_2HPO_4$	= 81.6	per cent.	(top) to	68	per cent. (bottom).
$Mg_3(PO_4)_2$	= 16.8	,,	,,	22.6	,, ,,
$Ca_3(PO_4)_2$	= 2.3	,,	,,	9.7	,, ,,

P_2O_5, 54-59 per cent.; K_2O, 28-40 per cent.; MgO, 6-8 per cent.; CaO, 1-4 per cent. Small amounts of chlorides, sulphates, etc.

Structure and Life Conditions of Yeast.—The ordinary beer yeast consists of minute egg-shaped single cells, about 0.01 mm. diameter. The cell consists of protoplasm enclosed by a cellulose cell wall and containing a spherical or disc-shaped nucleus, which can be made visible by staining. Vacuoles appear at the end of fermentation filled with a low-refractive fluid, also "granules" or "oil-drops" appear consisting of highly-refractive round or angular bodies. Besides vegetative propagation by budding, yeast also forms endospores under special conditions, the cell dividing into two to four spores which then germinate into new yeast cells. The spores of "culture" yeasts appear to be *empty*, while the spores of "wild" yeast are strongly refractive. Hansen has used the different spore formation to differentiate between the various types of culture and pure yeast.

Yeast is killed when heated in water to 75° C., but when dry will stand a temperature of +100° C. to −130° C. Cooling for months is not detrimental to yeasts. Drying in a finely divided condition kills yeast after a few days. Yeast causes alcoholic fermentation between 0° C. and 50° C. The optimum temperature is 28°-34° C. Yeasts retain their vitality longest in a 10 per cent. sucrose solution. Samples have been kept alive for over twenty years (Hansen) in this solution. A 22-25 per cent. sugar solution is completely fermented by most yeast races, but they refuse to grow in a 60 per cent. sugar solution. Yeasts require for their growth certain organic and inorganic salts, such as nitrogen compounds (amides, peptones), phosphates, sulphates, potassium, and magnesium salts—such are invariably found in grape juice and beer wort. Hence, although yeast will cause fermentation in a pure cane sugar solution, yet they cannot *grow* in this solution as the necessary

food stuffs are wanting. The presence of oxygen is also necessary in order to stimulate the first growth of yeast—hence the practice of blowing air through growing yeast.

Alcohol poisons yeast. In a solution containing only 5 per cent. by volume of alcohol, most yeasts cease to propagate. The enzymes in the yeast cell, however, are not much affected by this amount of alcohol, since some of the more powerful yeasts will generate a solution containing 18-19 per cent. alcohol, while wine yeasts have been known to ferment the solution until it contains 19 or 20 per cent. of alcohol. Nevertheless such yeasts cease to propagate in a solution containing more than 10-12 per cent. of alcohol. Distillery yeasts in concentrated mashes produce a solution containing usually 10-12 per cent. of alcohol. Fermentation is not likely to progress in a solution containing more than 20 per cent. by weight of fermentable matter.

Among yeast poisons are mercuric chloride, copper sulphate, phenol, formaldehyde, salicylic acid, hydrofluoric acid, sulphurous acid, carbon disulphide, chloroform, ether, and "antiseptics" generally (see p. 241). Free acids (especially the volatile fatty acids) and bases also exert a deleterious effect on yeast. Yeast, however, will bear the presence of a considerable quantity of lactic acid (see p. 235).

The Chief Yeast Races.—An enormous number of different races exist, each characterised by producing alcoholic liquors of different flavours and characteristics.* We may divide them into two great classes:—

(*a*) **Culture Yeasts**, *e.g.*, *S. cerevisiæ*, *S. ellipsoideus.*
(*b*) **Wild Yeasts**, *e.g.*, *S. pastorianus.*

(*a*) Culture Yeasts

Culture yeasts have been cultivated for long periods of time in the fermentation industries, and consequently have acquired characteristics which make them especially valuable for the production of alcoholic liquors.

We may classify culture yeasts thus:—

Saccharomyces cerevisiæ.—Top (high) yeast; bottom (low) yeast.
„ *ellipsoideus.*—Ferment of wine.

All these yeasts ferment the monosaccharides, also cane sugar and maltose, but not milk sugar.

Beer yeasts, distillery yeasts, compressed yeasts, and bakers' yeast all belong to the genus called *Saccharomyces cerevisiæ*, while yeasts for making **wine** belong to another genus, *Saccharomyces ellipsoideus.*

A yeast used for beer (brewery yeast) must generate certain substances possessing a characteristic aromatic taste or odour. It must also readily separate from the fluid, leaving a clear, bright liquid. A **distillery yeast**, on the other hand, must have a high fermenting power, in order to produce the maximum quantity of alcohol. A **baking yeast** should be rapid in action, and generate a large amount of alcohol and CO_2 in order to "raise" the dough. It should be noticed that a brewers' yeast is quite unsuited for use in a distillery, and *vice versâ.*

Beer Yeasts, Brewery Yeasts.—These must clarify well, raise a good head, and generate a pleasant taste in the beer. Two well-marked varieties of these occur, namely, **top-fermentation** and **bottom-fermentation yeast**. They are sometimes called "high" and "low" yeasts respectively, the reference here being to the temperatures at which fermentation is carried on with them. The **high** or **top-fermentation** yeast is used to ferment infusion beers, and is the variety used by **English brewers.** They rise to the surface of the fermenting liquid, and grow best between 28°-34° C. The **low** or **bottom-fermentation** yeasts is the variety which brewers of lager beer (Germany and U.S.A.) employ in the fermentation of decoction worts. They settle at the bottom of the fermenting liquor and ferment at a low temperature of 4°-10° C.

* Many wild yeasts do not cause alcoholic fermentation at all.

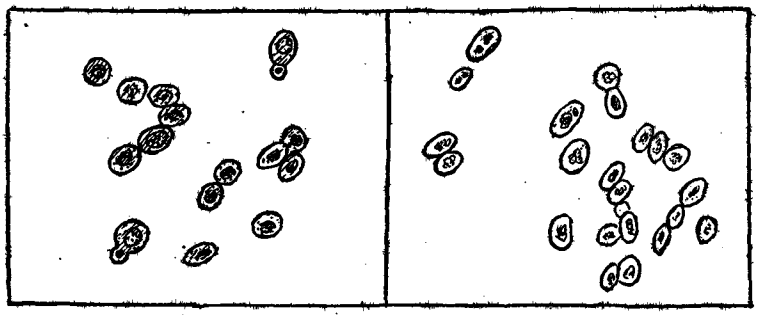
When working with this low temperature, fermentation proceeds much less rapidly than with high yeast; growth and reproduction proceed more slowly, and the budding gives rise to less extensive colonies of cells; but the beer thus produced is usually richer in CO_2 than that produced at a higher temperature.

The following are the chief brewery yeasts:—

Top Yeasts.—*Saccharomyces cerevisiæ*, Hansen, from English and Scotch breweries, a vigorous beer top yeast. **Yeasts** for making **English Porter, Stout, Ale, Berliner Weissbiere, Lichtenhainer Beer, Braunbiere, Malzbiere.** The Institute for Gärungsgewerbe at Berlin breed two "top" yeasts, namely "Hefe A," a weak fermenting yeast, and "Hefe B," a powerful fermenting yeast.

Bottom Yeasts.—The following are the two chief types of German "bottom" yeasts: (1) Hefe "Frohberg"; (2) Hefe "Saaz." Between lie many intermediate varieties. Hansen (Copenhagen) cultivates **Carlsberg Bottom Yeast 1**, which produces a very stable beer, not readily clarifying, and **Carlsberg Bottom Yeast 2**, producing a beer not so stable as from 1, but clarifying more readily.

Distillery Yeasts.—These are top-fermentation yeasts. Distillery yeasts must cause a quiet but rapid fermentation, with formation of a high percentage of alcohol. They must be able to withstand a considerable amount of free acid, since the fermentation usually proceeds in fairly strongly soured solutions. It is not necessary that they should clarify well and raise a good head—in this they differ from brewery yeasts, where these are points of great importance.



Top-Fermenting Ale Yeast. Bottom-Fermenting Lager Yeast.

FIG. 85.

The most important pure **distillery yeast** is **Race II., Berlin,** which was isolated in 1889 from a distillery in West Prussia. Suitable for fermenting highly concentrated mashes, possesses great power of resistance to high alcoholic content. For distilleries which ferment **molasses** and sugar refuse, characterised by a high percentage of various salts, the best yeasts to use are certain **wine yeasts.**

Yeasts for Manufacturing "Compressed Yeast."—"Compressed yeasts" are used by bakers for incorporating into dough. The CO_2 gas generated by the fermentation, and also the alcoholic vapours when in the oven, puff up the bread and make it light. Bakers' yeast must have a pleasant taste and smell, develop rapidly and generate much CO_2 and alcohol. It should also not be too sensitive to acid. **Berlin Race V.** is largely used for the manufacture of compressed yeast, also **Berlin Race XII.** is very suitable.

Wine Yeasts.—All belong to the species *Saccharomyces ellipsoideus.* These are found in very large quantities on ripe grapes, whence they get into the expressed grape juice or "must" and by fermenting the grape sugar present, convert it into wine.

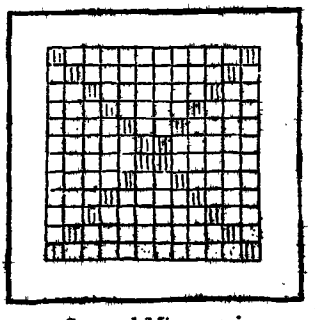
An enormous number of distinct races occur, each one producing a wine of a different flavour. Each different wine district, in fact, possesses characteristic and distinct races of *Saccharomyces ellipsoideus*, and thus it comes about that wines from different districts, and even wine from the

same district but from different vineyards, can be readily distinguished by experts merely by their various tastes and bouquets.

Strictly speaking they are "wild" yeasts, since they occur free in nature, and have not, until quite recently, been systematically cultivated like brewery and distillery yeasts. Recently, however, pure cultures have been grown, capable of producing wine of definite specific characteristics. We prefer, therefore, to discuss their properties here as "culture" yeasts.

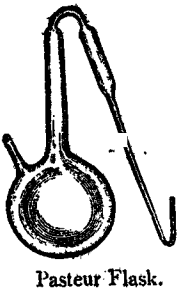
Saccharomyces ellipsoideus, T. Hansen, is a wine yeast, found by Hansen on the surface of ripe grapes in the Vosges district. The cells have an ellipsoidal shape. It is a bottom yeast, and ferments saccharose, dextrose, laevulose, and maltose, but not lactose. The different races of this variety not only produce wines of very different tastes and bouquets, but also exhibit very important differences as regards the amount of alcohol produced, and the way in which the fermentation proceeds. Some of these races actually manage to exist in a 60 per cent. sugar solution—a property made use of in the production of "Melton Wine." In concentrated sugar solutions they produce much more alcohol than the species *Saccharomyces cerevisiæ*. In some cases they produce liquids containing 20 per cent. of alcohol (see p. 244).

Freudenreich Flask.



Squared Microscopic Cover-Glass.

Böttcher Moist Chamber.



Pasteur Flask.

FIG. 86.—Apparatus for Pure Yeast Culture. Hansen's Method. (J. Griffin & Sons, London.)

Other Yeasts. — *Saccharomyces pyriformis* (Marshall Ward) produces alcoholic fermentation of English ginger beer. Used in conjunction with the "ginger-beer" plant, *Bacterium vermiforme*. *Saccharomyces mali*, Du Clauxi, Kayser, from **cider**, ferments invert sugar and produces esters (bouquet).

Schizosaccharomyces pombe, the yeast in pombe (Negro millet beer), ferments dextrose; used in South American distilleries; *Schizosaccharomyces mellacei*, in Jamaica rum.

(*b*) Wild Yeasts

The "**wild**" yeasts occur free in nature; they are not cultivated systematically like ordinary brewery or distillery yeasts, usually because they possess unpleasant characteristics and, indeed, often set up various "diseases" in beer, or affect the fermenting power of infected yeasts. Thus *S. pastorianus I.* produces a bitter taste in beer, while *S. pastorianus III.* produces cloudiness. They occur as sausage-shaped cells. *Saccharomyces ellipsoideus II.*, Hansen, is a dangerous disease yeast for breweries, causing turbidity.

The "**Kahm**" **yeasts** (*Kahm Hefe*), *e.g.*, *Mycoderma cerevisiæ* and *vini*, consisting of round or elongated cells, form a skin on the surface of the fermenting liquor. They require oxygen; and can produce from sugar a small percentage of alcohol, but usually oxidise the alcohol directly to CO_2 and water, with the rapid absorption of oxygen. *S. exiguus* (from compressed yeast) ferments monosaccharides and cane sugar, but not **maltose**. *S. apiculatus* also ferments only monosaccharides. Both are useless for the brewery. *S. ilicis* (bottom yeast) and *S. aquifolii*, Grönland, produce a bitter and disagreeable taste in worts.

S. membranæfaciens, Hansen, found in wines and polluted waters. Generates **acids** from sugar. Propagates in presence of 12 per cent. alcohol. Destroys the bouquet of wines.

Certain **Moulds** also possess the power of fermenting sugar, *e.g.*, *Mucor racemosus* (see under **Moulds**).

Pure Cultivation of Yeast

Hansen's Method of Pure Yeast Culture from a Single Cell.—The individual yeast cells in a drop of fresh yeast are separated by thoroughly mixing twice in succession with sterilised water contained in Freudenreich flasks (see Fig. 86). A drop of the mixture is then transferred to a Freudenreich flask containing liquefied wort gelatine, and thoroughly mixed. A drop of the wort gelatine mixture is then spread in a thin layer on a squared microscopic cover-glass, left until set under a bell jar, then placed, gelatine film downward, over small moist chambers, called Böttcher chambers, containing a drop of water at the bottom of the cell. The slide is examined under the microscope and the positions of a number of individual yeast cells, which are several millimetres apart from other cells, are carefully marked. The culture is then kept in an incubator at 20° C. (68° F.). Each cell develops into a colony of cells. When the colonies are large enough a pure culture in sterilised wort is obtained by inoculating from each separate colony nutrient sterilised wort contained in a Pasteur's flask. In this way an absolutely pure culture is obtained from a single cell; these separate cultures are then examined as to their action on wort and the most suitable species selected for use in practice. The culture yeast is then transferred to larger quantities of a nutrient wort. The production of large quantities of pure cultivated yeast is accomplished in special pure culture apparatus (see below).

Lindner's Method of Drop Culture is a slight modification of Hansen's. He dips a pen into the diluted yeast, and draws a line with this on the under side of a sterilised microscopic slide, which is then fastened by means of vaseline on the hollow moist chamber for observation under the microscope. As the individual cells develop they are used to inoculate larger quantities of sterilised wort contained in Pasteur's flasks, as in Hansen's method. The method is easier than Hansen's, and the yeast cells can be more easily recognised.

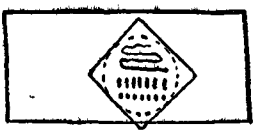


FIG. 87.—Lindner's Method of Drop Culture.

Apparatus for the Industrial Production of Pure Culture Yeast

Hansen's Apparatus.—The apparatus consists of three parts, viz.: (1) The air-pump A with the air reservoir B. (2) The wort cylinder D. (3) The fermentation cylinder C (see Fig. 88).

By means of the pump A air under a pressure of 3·4 atmospheres is forced into the air reservoir B, which is provided with a manometer and a safety-valve. The wort cylinder D is now sterilised with high-tension steam from the brewery boiler, which drives out all contained air through the pipe *n*, the end of which is covered by water in *o*. Next, the compressed air from B is allowed to rush into D, passing on its way through the cotton-wool filter *m*, which removes all germs. Boiling wort is now run into D through the pipe *u*. The wort is cooled to the proper temperature by means of a pipe *pp*, which sprays cold water over the surface of D. The proper amount of sterilised air for aeration is introduced through the cotton filter *m*. The fermentation cylinder C is now sterilised in exactly the same manner as D by means of tension steam. C is also supplied with sterilised air through the cotton-wool filter *g*, while a glass tube *ff*, connected with the cylinder by the pipes *e* and *h*, allows the level of the wort in C to be readily ascertained. A small pipe J and an indiarubber tube allows a small amount of pure yeast culture from a Pasteur flask to be introduced when required into the sterilised wort in C. The introduction of yeast need only be made once, when it develops in the wort and gives a continual supply of yeast for a year or more. The outlet tap *l* is arranged so that no infection from without can enter the interior of C. To ensure against this danger a considerable pressure of air in C is always present. The tube *kk* places the cylinders C and D in communication, and allows the transfer

of sterilised wort from D to C as required. When the level of liquid in C (as seen by the glass tube *ff*) nearly reaches J, the tap *k* is turned off, the yeast culture added through J, J is shut, *k* opened again, and the addition of wort from D continued until C is nearly filled (up to a mark on the glass tube), and the mass well stirred by the rousers *bbb*. In this way about 220 litres of wort is placed under fermentation, with an absolutely pure yeast culture. After about ten days the beer formed is drawn off through the outlet tap *l*, compressed air being simultaneously allowed to enter through the filter *g*.

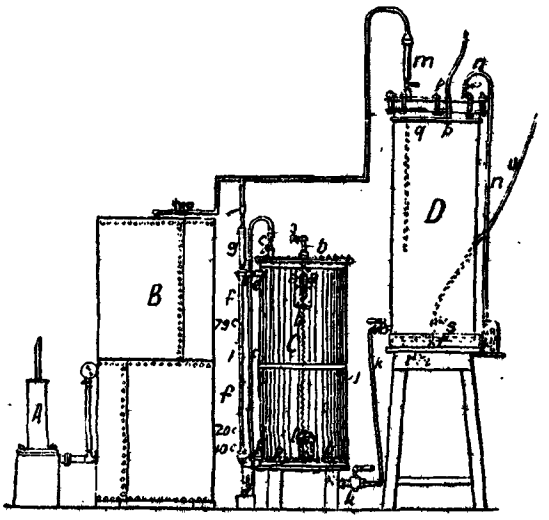


FIG. 88.—Hansen's Apparatus for Pure Yeast Culture. (By permission of The Review Press Ltd. From Jörgensen's "Pure Yeast Management.")

This operation is carried out as follows: First of all some of the dregs are allowed to run out through *l*, then *l* is closed, wort added until C is again filled to the mark (as seen in the glass tube *ff*), stirred, and then 27 l. of beer and yeast are run off through *l*. More wort is added, stirred up, and another 27 l. run off. The volumes run off are indicated by marks on the glass tube *ff*. The 54 l. of yeast liquid so obtained contain enough yeast to ferment 8 hectolitres of wort. The rest of the yeast, still contained in C, is allowed to ferment another 220 l. of wort from C, and can be again drawn off as before. In this way a continuous supply of pure yeast culture can be obtained from C.

Lindner's Small Pure Yeast Culture Apparatus.—This is capable of producing 1 kg. yeast. The apparatus consists of a cylinder A and a flask B, which is connected up through the safety bottle C with an ordinary filter pump D. 50-60 l.

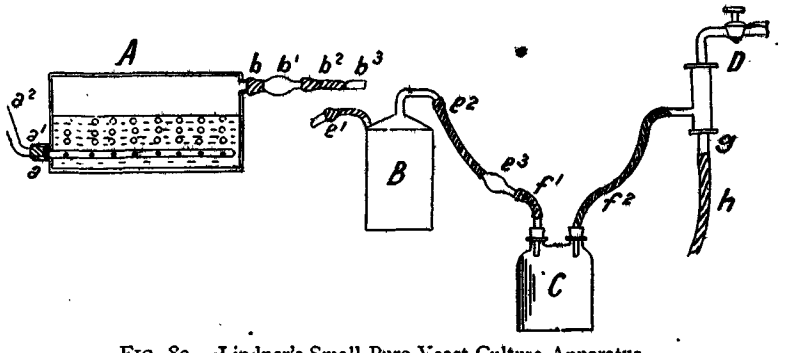


FIG. 89.—Lindner's Small Pure Yeast Culture Apparatus.

of wort are sterilised in A and caused to ferment by a pure yeast culture contained in B, while air is sucked through the apparatus by means of D, A and B being joined up together for the purpose. The incoming air is sterilised by passing through a sterilised (at 150°-160° C. in air oven for two hours) cotton-wool filter attached at a^2. e^3 is another such cotton-wool filter to prevent infection reaching B.

Lindner's Large Pure Yeast Culture Plant.—This consists of the large sterilising and fermentating copper cylinder A and the culture yeast flask B (or C). A number of tubes lead into A, by means of which steam, water, wort, or air can be introduced. The contents can be agitated by means of a sterilised air blast which is passed in through the coil *d*. The wort in A is sterilised by tension steam, cooled, impregnated with pure culture yeast from B, and, when sufficient yeast has grown in A, the contents are emptied through *i* and *e*, leaving, however, sufficient fluid in the apparatus to fill B, so as to have a supply of the same kind of yeast so as to start the operation over again when A is again refilled with sterilised wort.

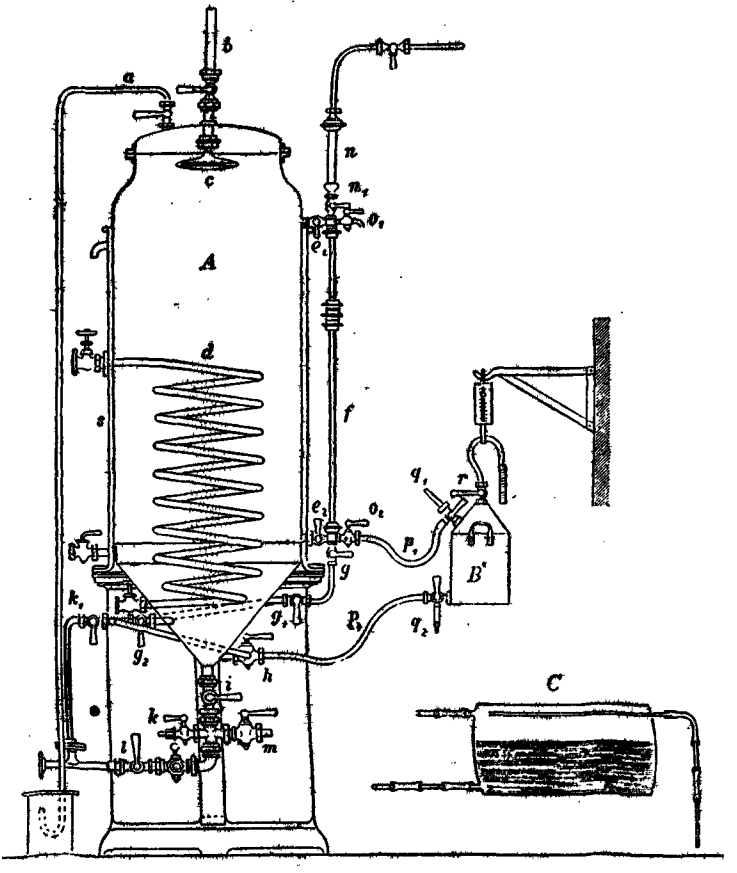


FIG. 90.—Lindner's Large Pure Yeast Culture Plant.
(Manufactured by F. W. Pest, Berlin.)

Hansen was the first to introduce the production and application of pure culture yeast in **bottom-fermenting** breweries, and his methods have abolished all empiricism and replaced it by absolutely safe working methods in practice.

Jörgensen since 1885 has applied the pure culture of **top-fermenting** yeast, but the success in practice has not been so marked as with the **bottom-fermenting** varieties (see under **Beer**).

It should be noticed that pure culture alcohol yeast is not only free from all disease-producing germs, but consists of *one single species only*. It is used as a "pitching" yeast in the brewery. As soon as the biological tests and control show any deterioration of the pitching yeast, it is discarded and is replaced by the new pure culture yeast, which is kept continually growing in the pure culture apparatus. The pitching yeast is thus periodically replaced by pure culture yeast. Nevertheless, in the course of time the pure culture yeast itself may begin to degenerate, owing to its progressive alteration into species of yeast exhibiting undesirable properties, the fermenting liquor developing

a *flavour* different to the normal one in this case. When this occurs it will be found that *not all the cells degenerate simultaneously*—some are unchanged. Consequently a sample of the yeast is taken and a dilution made, the individual cells being well separated from one another, and a comparative series of fermentations made with the different individual cells show that there are differences between these cells. Some of the new growths will show the newly developed disagreeable characters, but others will be found to be cells which have not changed their character. Pure single cell cultures are then made from the unchanged varieties, as previously described, and a culture obtained similar to the original.

Manufacture of Compressed Yeast

Bakers use yeast extensively for mixing with the dough. It generates CO_2 and alcohol from the dextrose and maltose formed in the bread during the raising and kneading process. In baking, the alcohol assists the CO_2 in causing sponginess of bread owing to its vaporisation* during the heating. Bottom-fermenting yeast is too slow in action and bitter for this purpose, while ordinary brewery yeasts (top) are also not suitable on account of their "hop" flavour. The species now used is a distillery top yeast, and, being sold in a compressed state, is known as "compressed yeast."

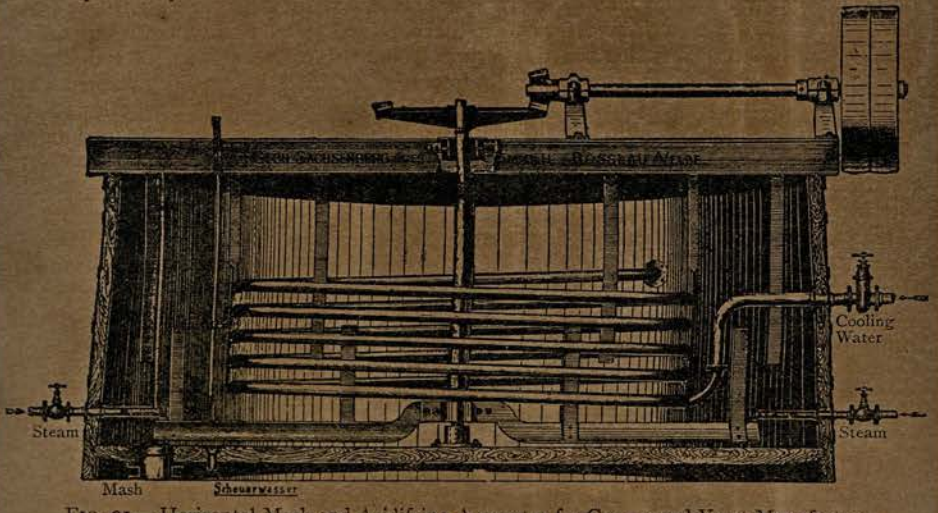


FIG. 91.—Horizontal Mash and Acidifying Apparatus for Compressed Yeast Manufacture. (Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

Compressed yeast manufactories are always grain distilleries, and, indeed, are the largest of this kind. Thus one of the largest compressed yeast manufactories in the world, Helbing of Hamburg, produces yearly 2,500 tons of compressed yeast, 25,000 hl.† of alcohol (100 per cent.) in the form of spirits, etc., and, daily, 2,000 hl. of spent wash, which is partly used fresh as a cattle food, and partly sold in a dry state. The Fleischmann Manufacturing Company, U.S.A., is another enormous concern of the same kind. To show the magnitude of the industry we may mention that in 1904-5 Germany alone produced 36,730 tons of compressed yeast (1,350 tons being exported to England) and 482,000 hl. alcohol (100 per cent.).

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* **Baking Powder** is used as a substitute for yeast, a chemical generation of CO_2 gas causing the dough to rise.

A common baking has the composition: 34 sodium bicarbonate + 25 cream of tartar + 40 starch. Use 15-20 parts to 500 parts flour. For cakes use 1 sodium bicarbonate + 2 cream of tartar + 15 flour, or 10 sodium bicarbonate + 7.5 tartaric acid + 17 starch. In bread making sometimes dilute HCl (or calcium biphosphate) is mixed into the dough and then sodium bicarbonate is stirred in.

A common "self-raising" flour is: 10,000 wheat flour + 190 cream of tartar + 85 sodium bicarbonate.

† 1 hl. = 1,000 litres = 220.1 gallons.

Compressed yeast is produced by two different methods, viz., the "old" method, such as is used in ordinary distilleries, and the modern and more economical "aeration method."

Old Method for Producing Compressed Yeast.—A mixture of malt and 1-5 parts rye or wheat are mashed (see under **Spirits**) at a convenient temperature, so as to obtain as complete a transformation as possible of the starch into maltose. The mash is allowed to stand in the vat (Fig. 91) at about 35° C., the temperature most suitable for the production of lactic acid. The lactic acid bacteria rapidly multiply—in modern practice pure lactic acid bacteria are sometimes added—and a marked acidulation develops. The lactic acid organism is peculiarly sensitive to its own product, and ceases to develop after 1.5 per cent. of lactic acid has been formed. The presence of lactic acid prevents the undue development of bacteria and wild yeasts, also it peptonises the nitrogenous matters of the grains in the mash so as to render them available as yeast foods. Sufficient acidulation being produced the mash is cooled to 25° C., yeast is added, and fermentation allowed to proceed for ten to eighteen hours.

When the yeast is "ripe"—*i.e.*, when it has ceased to grow, and so is free from small daughter cells—and when most of the yeast has been forced to the surface of the liquid by the CO_2, the yeast is skimmed off from the surface of the liquid, filtered through fine gauze in order to free it from malt husks, etc., washed with cold water, and pressed in *filter presses* The mash remaining is allowed to ferment with the yeast still left in the liquid for about twenty-four hours longer, and then is distilled for alcohol.

New Aeration Method of Manufacturing Compressed Yeast.—This process makes use of the fact that yeast requires oxygen for its full development; it differs from the previous method in that clear filtered worts are used for fermentation so that practically all the yeast formed is isolated.

The mash contains more maize and less rye than in the old process, and contains a considerable amount of the nitrogen-rich malt germ and green malt. The mash is allowed to sour (as before) with lactic acid, up to 0.6 per cent., at 50° C., is sterilised at 65° C., filtered, cooled to 30° C., and pitched with yeast. The fermentation takes place in vats (Fig. 92) through which a continual and powerful stream of air is forced from perforated tubes at the bottom of the vat, while the temperature is maintained at 30° C. by a heating coil. After twenty-eight hours or so the sugar is all fermented, and the yeast ceases to grow, *i.e.*, becomes "ripe" and free from budding cells. The yeast is then separated from the clear fermented liquor, by passing through centrifugal machines (Fig. 93) (Laval separators), similar to those

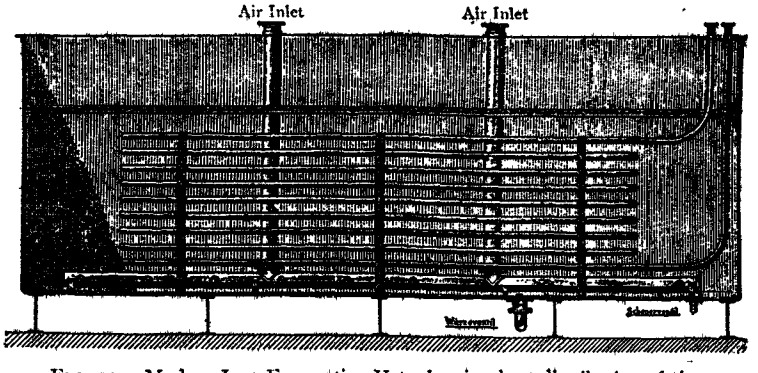

FIG. 92.—Modern Iron Fermenting Vat, showing best distribution of air for Aerated Yeast Manufacture.
(Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

used for separating cream from milk, and is then pressed dry in filter presses, sometimes with the addition of starch. The clear residual mash is then distilled for alcohol (see **Spirit Distillation**).

By this process 100 kg. of grain yield 23 kg. of good compressed yeast containing 70 per cent. water and 18 l. of 100 per cent. alcohol. Under favourable conditions over 30 kg. yeast and 15 l. alcohol are obtainable. The old process only produced 14 kg. yeast but more alcohol, viz., 28 l.

Although the presence of air favours the development of wild yeasts and bacteria, the initial souring of the mash prevents their development to any serious extent, and "aerated" yeast is now quite as energetic a raising agent as the best yeast as manufactured by the older process. Nevertheless the mother yeast, from which the crop is raised, is usually bred by the older process.

FIG. 93.—Yeast Centrifugal Separator with Steam Turbine. (Made by Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

Formerly it was the custom to add to the yeast a certain amount of starch before pressing, as a drier product with better keeping powers was thus obtained. The modern yeast races used, however, are now so improved that they are no longer "slimy," and are easily pressed dry; consequently starch is now no longer necessary. If added (especially if for lowering the price of the product) its presence and amount should be stated on the label.

Compressed yeast will keep a long time when securely packed (best in tinfoil) and kept at 8°-12° C. But when exposed to air or in warm weather it rapidly becomes stale and deteriorates. Completely dried yeast will keep for years, but is lacking in fermentative power. The ultimate aim of the yeast manufacturers, namely, the propagation and growing of the yeast without the simultaneous production of spirits, has not yet been achieved, although it is, perhaps, a theoretical possibility.

Statistics.—In 1910 England imported 203,900 cwt. of yeast of value £394,121. Of this quantity the Netherlands supplied 106,500 cwt., Belgium 48,500 cwt., France 26,000 cwt., Germany 18,600 cwt. The United States in 1910 exported $71,000 of yeast, Canada taking $55,000. Germany produces annually about 800,000 cwt. of yeast.

Chemical Analysis of Yeast

The yeast, which should have a pleasant aromatic smell, is first examined under the microscope (600-800 power), and the form, shape, and size of the cells observed. Old yeast differs in appearance from young yeast. The number of dead cells present are ascertained by adding to the solution

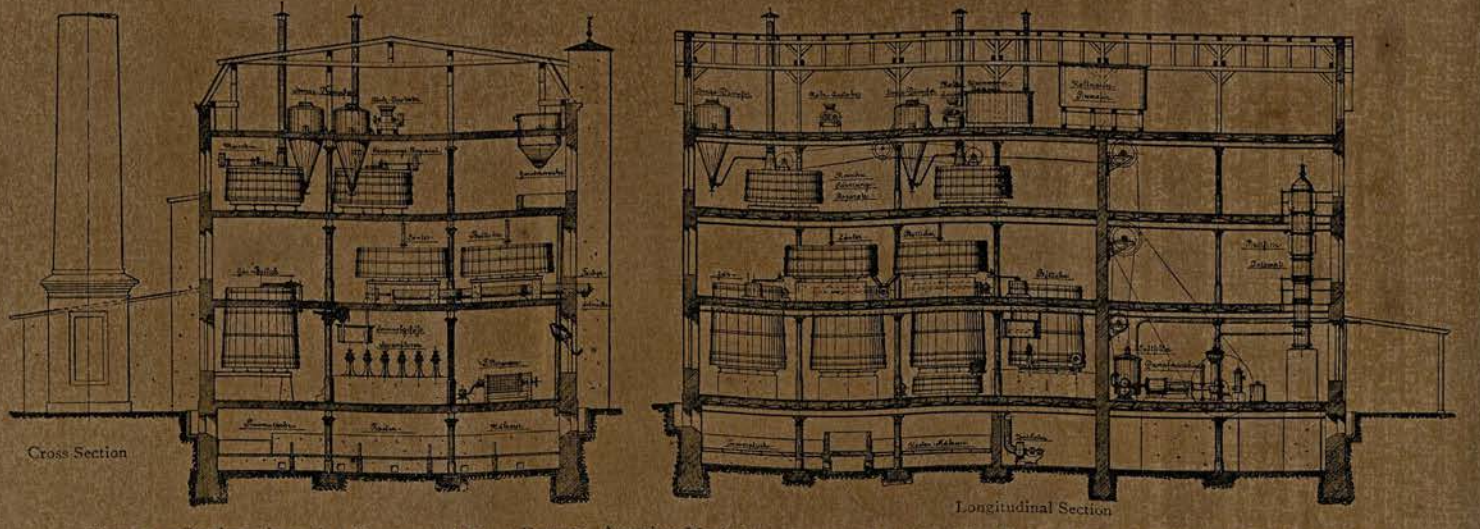

FIG. 94.—Sections through a Compressed Yeast Factory, Aeration Method. (Designed by Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

a drop of methyl violet, eosin, or fuchsine in alcohol. Dead cells stain, but living ones are unaffected. The presence of bacteria, etc., may be detected by their different shapes. Next, the detection of wild yeasts is carried out by using Hansen's method of **spore culture** on blocks of sterilised gypsum (see Jörgensen's "Practical Yeast," p. 9).

The difference between the spores of "culture" yeasts and "wild" yeasts is so great that one quickly notices it on placing the slide under the microscope. The water and ash of a yeast are determined according to the standard methods of food analysis.

The **fermenting power** of a yeast, *i.e.*, the rapidity with which it decomposes sugar, turning it into CO_2 and alcohol—is especially required for the valuation of compressed yeast. **Meissl's Method** determines the *weight* of CO_2 which is generated by 1 g. of yeast within six hours at 30° C. from a solution in ordinary tap water of 400 g. pure sucrose, 25 g. ammonium phosphate, and 25 g. potassium phosphate. A yeast generating in this time 1.75 g. CO_2 is stated to have a *fermentative* power = 100 and be a "normal one."

Hayduck and **Kusserow's** methods measure the *volume* of CO_2 generated by a given quantity of yeast in a certain sugar solution. For details see the special works referred to above; also Dr Slator's article below.

The amount of starch present—which may vary from 5-50 per cent.—is estimated in the usual way.

II.—THE RATE OF ALCOHOLIC FERMENTATION BY LIVING YEAST

By Arthur Slator, D.Sc., Ph.D.

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" "The Mechanism of Alcoholic Fermentation." *Journ. Chem. Soc.*, 1908, **93**, 217.

" "Über Zwischenprodukte der alcoholischen Gärung." *Ber. deut. chem. Gessel.*, 1907, **40**, 123.

" and H. J. S. Sand.—"The Rôle of Diffusion in Fermentation by Yeast Cells." *Journ. Chem. Soc.*, 1910, **97**, 922.

" "Estimation by Fermentation with Yeast." *Journ. Soc. Chem. Ind.*, 1908, **27**, 653.

" "The Rate of Alcoholic Fermentation." *Journ. Inst. Brew.*, 1911, **17**, 147.

The rate of fermentation by living yeast depends on certain factors which have been fairly accurately determined. An excellent account of the matter is given in Dr A. Harden's monograph on "Alcoholic Fermentation" (London, 1911) to which the reader is referred for further particulars.

A convenient apparatus for measuring such rates is shown in the accompanying figure.

A glass bottle of about 150 c.c. capacity is fitted with a rubber bung and connected by pressure tubing to a mercury manometer which can register pressures from a vacuum to about 30 cm. of mercury. The apparatus can be exhausted and kept air-tight by means of a side piece and a stopcock.

The fermenting solution is introduced into the bottle, and the apparatus is then exhausted. The bottle, which rests in a thermostat, is shaken at definite intervals of time, and the amount of fermentation is measured by the change in pressure. To assist in the shaking twenty glass beads of about the size of peas are placed in the bottle. The apparatus can be calibrated by fermenting completely 0.1 g. dextrose in the bottle and observing the corresponding change in pressure.

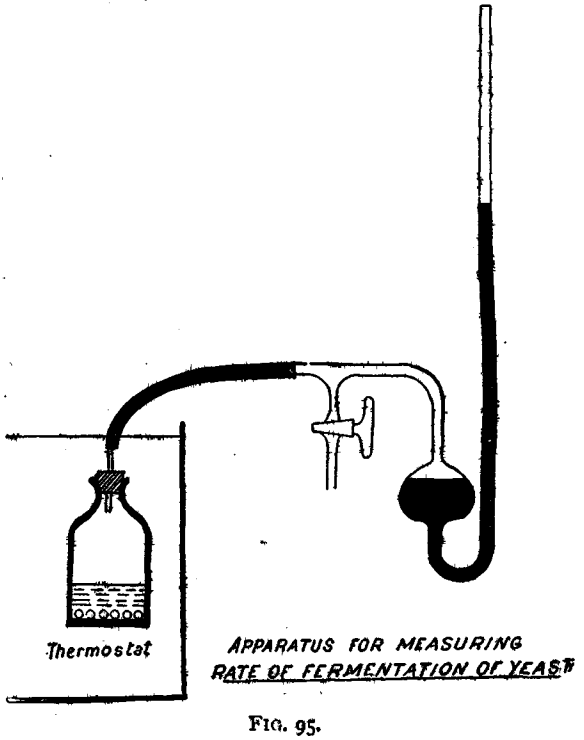

FIG. 95.

The Rate of Fermentation of Dextrose.—The factors which influence this rate have been determined by making up definite solutions of dextrose and adding yeast in known amounts. The liquid is transferred to the bottle of the apparatus and the initial rate of fermentation measured in the manner described.

The rate of fermentation of dextrose is almost independent of the concentration of the sugar if the solution is not too concentrated or too dilute.

The rate of fermentation is exactly proportional to the amount of yeast present.

It can be shown that the diffusion of the sugar into the yeast cell takes place so rapidly that the yeast cell is efficiently supplied with sugar even at very dilute concentrations.

The influence of temperature on the rate of fermentation is very great. The activity of a yeast cell is almost entirely dependent on the temperature, and it is possible to construct a table showing the activity of a yeast cell at various temperatures.

The following table refers to a brewery yeast. The activity column gives the number of grams per second fermented by 10^{14} yeast cells.

Temperature. °C.	Activity.	Temperature. °C.	Activity.
40	5.05	20	1.30
35	4.05	15	0.68
30	3.00	10	0.345
25	2.08	5	0.14

The Rate of Fermentation of Different Sugars

Laevulose is fermented by various yeasts at the same rate as dextrose.

Mannose is probably fermented by all yeasts which ferment dextrose, but the two rates differ—in some cases dextrose is fermented more rapidly than mannose, in other cases the reverse happens.

Fresh samples of yeast ferment mannose more rapidly than dextrose, but by older samples the glucose is more rapidly decomposed.

Galactose.—Only certain species of yeast are capable of fermenting this sugar, even though they ferment dextrose, laevulose, and mannose readily. The special interest in the fermentation of this sugar consists in the fact that even these special yeasts cannot ferment the sugar unless they have previously been acclimatised by growth in the presence of galactose.

Sucrose (cane sugar) can only be fermented by yeasts which contain the enzyme "Invertase," which converts the sugar into dextrose and laevulose (invert sugar). Most culture yeasts contain this enzyme and are capable of fermenting sucrose as rapidly as dextrose. The invert sugar is produced more rapidly than it is fermented, and so accumulates in the fermenting solution.

Maltose is fermented by yeasts which contain the enzyme "Maltase." This enzyme is also present in most yeasts used technically, and such yeasts ferment maltose almost as rapidly as dextrose.

Lactose.—A few varieties of yeasts contain the enzyme "Lactase" and ferment lactose (milk sugar).

Glycogen.—The autofermentation of yeast consists in the transformation of the glycogen in the yeast cell to alcohol and carbon dioxide. The rate of the autofermentation depends on the amount of glycogen in the yeast cell, which varies according to the age of the yeast. With fresh yeast the rate is about one-tenth the rate of the fermentation of dextrose, with older samples the rate may fall to one-fortieth of the value.

Malt Wort.—The rate of fermentation of malt wort (p. 273) during the first part of the fermentation is the same as that of dextrose. The temperature and the number of yeast cells are therefore the main factors which determine this rate.

Malt wort contains the necessary food for yeast growth, and the amount of yeast increases for some time after seeding. The number of yeast cells depends, therefore, on the seeding and the growth which has taken place. Yeast growth

does not continue indefinitely but attains a maximum which was found by A. J. Brown to be approximately independent of the amount of the seeding.

In all probability it is the changes in the medium caused by the yeast which determines this maximum growth. Thus the sugars which are necessary to yeast growth are transformed to alcohol and carbon dioxide, both of which inhibit yeast growth, and when this transformation is partly completed the yeast growth stops. This explanation also makes it easy to understand how different seedings have little influence on the final crop. If we consider two worts seeded with yeast one ten times the amount of the other, then if these concentrations are small compared with the final yeast crop the growth in the first case from one to ten is accompanied by hardly any change in the medium. The two would then be almost identical and produce the same final yeast crop.

The Retarding Influences of Antiseptics.—Many substances, such as mercuric chloride, copper sulphate, phenol, salicylic acid, and many others, on addition to a fermenting solution, inhibit the reaction. These substances on addition in very dilute concentration are said to accelerate the reaction. It can be shown, however, that this acceleration is on the growth of yeast and not on the fermentation.

Phosphates which have such a remarkable accelerating influence on fermentation by yeast juice have no such influence on fermentation by living yeast (see p. 222).

Intermediate Compounds in Fermentation.—Chemists have long held the opinion that dextrose is first converted into some intermediate compound before the formation of alcohol and carbon dioxide. A compound of the formula $C_3H_6O_3$ has been suggested, and the fermentation equation then reads—

$$C_6H_{12}O_6 = 2C_3H_6O_3 = 2C_2H_5OH + 2CO_2.$$

Lactic acid and dihydroxyacetone both have this formula and both have been suggested as possible intermediate compounds. The lactic acid theory has been abandoned owing to general recognition that it is not fermentable. The slow rate of action of yeast on dihydroxyacetone makes the second suggestion also improbable.

III.—WINE

By G. Martin, Ph.D., M.Sc.

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Wine is an alcoholic fluid prepared without distillation by the fermentation of grape juice. The fermentation takes place spontaneously under the influence of special wine yeasts (*Saccharomyces ellipsoideus*) which occur naturally on grape skins and in the air.

The **vine**, *Vitis vinifera*, grows freely in Europe, Asia, and America. It requires an average temperature of 10°-11° C., and an average summer temperature of 18°-20° C.; while ripening it requires much sunshine in order that sugar may be formed. A climate with hot summers and severe winters is often very favourable for the cultivation of the vine. During the growth, rain is necessary, but when ripening only bright sunshine should reach the fruit. The weather has a very great influence on the growth of the vine. The soil is not so important, but warm loose soil—especially volcanic soil—is best. The soils must be rich in potash. The best vines are grown along the banks of the Rhine, in Southern Italy, in the Greek Islands, Spain, Austria, Southern France, Australia, Asia Minor, etc. France produces the largest quantity of wine, producing on an average 45,000,000 hl. annually, in value over 1,000,000,000 francs. Then follow, in order, Italy, Spain, Austria-Hungary, and Germany. In **Asia Minor** the vine is very extensively cultivated, but is utilised principally for the production of **raisins** (dried grapes).

It should be noticed that grapes are used not only for the production of wine, but also for the manufacture of **raisins** (dried grapes), in the manufacture of genuine grape sugar, of cognac brandy, wine-vinegar, etc. From **wine lees** are obtained tartar and tartaric acid; an oil is obtained from the seeds.

The riper the grape the more sugar it contains, and the richer in alcohol the resultant wine; consequently the grapes are never gathered until perfectly ripe, when it then contains, usually, 15-20 per cent. of sugar, and in exceptional cases 10-30 per cent. sugar. The sugar is a mixture of dextrose and laevulose, no sucrose (cane sugar) being present. The amount of free acid in the juice varies from 2.9 per cent. (unripe) to 0.9 per cent. (ripe), the acids being tartaric and a small amount of malic.

Pressing the Grapes.—The hard and sour grapes begin to become soft and sweet towards the end of August; at the end of October or beginning of November the sugar is at a maximum, and the grapes are plucked and pressed.

This latter operation is carried out by placing them in a wooden tub and stamping with a wooden maul or pestle to extract the juice. Sometimes they undergo instead a preliminary crushing by foot, other times they are ground in grape mills with wooden rollers.

If **White Wine** is required the juice is rapidly pressed away from the grape skins, stalks, etc., in special wooden presses. The best presses are the screw presses made of wood or cast iron. The clear juice runs through holes in the floor into the wooden fermenting vats.

If **Red Wine** is required, the stalks are carefully separated from the grapes, which are then macerated, and the mass allowed to ferment. When this occurs the alcohol generated extracts the red colouring matter from the fermenting grape skins, and the liquid acquires the fine red colour characteristic of red wine. Simultaneously a considerable amount of tannic acid enters the fluid.

It should be particularly noticed that *purple* or *red* grapes if pressed away from skins *before* fermentation yield a **white wine**. The red colour is only obtained when the skins are left in contact with the fermenting liquid for a suitable time—several days—and the liquid is then pressed away from the residual grape skins.

100 parts of grapes yield 60-90 parts of **must**, as the grape juice is called. The richest grapes are the first to yield juice when placed in the press. The juice

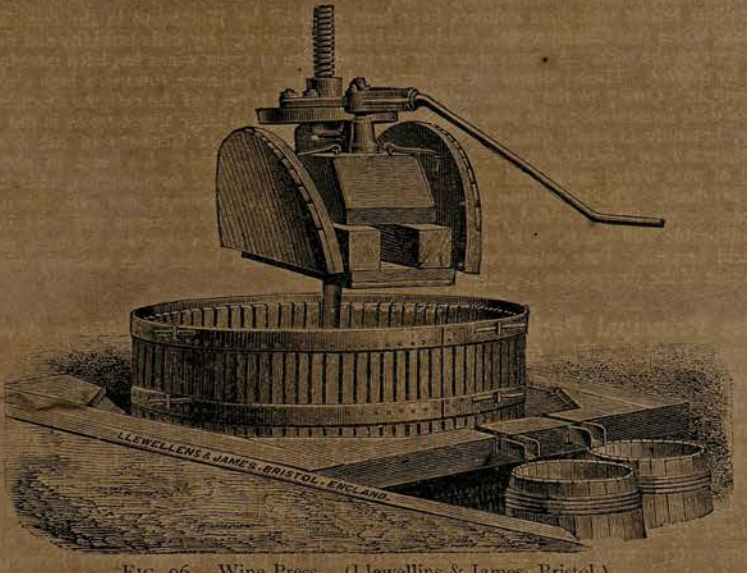

FIG. 96.—Wine Press. (Llewellins & James, Bristol.)

obtained from the first pressing produces the best wine—the so-called "first wine." The second pressing, using greater pressures, yields a **must** containing more acid, and from this is obtained the "press-wines." The third pressing yields the "after-wines." The residue or "marc" (German, *Treber* or *Trester*) is sometimes treated with water to yield an inferior wine.

1,000 parts of ripe grape juice (must) contain, on an average :—

Water	860-830 parts
Sugar (dextrose and laevulose)	150-300 ,,
Pectin, gums, colouring matter, albuminous matter, etc.	30-20 ,,
Ash	2-7-4 ,,

100 parts of the ash contain :—

Phosphoric acid	16-14 ,,
Potash	64-71 ,,
Magnesia	5-2.5 ,,

Fermentation of the Grape Juice.—The grape juice begins to spontaneously ferment within a few hours owing to the rapid development of wine yeasts. These

occur on the grape skins and stalks. They find their way naturally into the juice, and there rapidly develop, since the must contains a considerable amount of nitrogenous proteid matter and mineral salts which serve as an excellent food for the developing cells. In the more southern countries the fermentation proceeds between 15°-30° C. and is a **top fermentation**. Along the Rhine and in colder countries usually a **bottom fermentation** takes place at 10°-12° C. in special wine cellars. As in the case of beer, the higher the temperature of fermentation the more rapidly it takes place; the best products, however, are obtained at moderate temperatures.

The yeasts (see **Wine Yeasts**, p. 230) consist of various races of *Saccharomyces ellipsoideus*, and, naturally, those races which resist best a high alcohol and acid content come to the front and overpower inferior races.

For many years **pure wine yeast** culture has been introduced into the wine industry. Wortmann proved that different **wine yeast** types yield very different products as regards taste, bouquet, and acidity. Nevertheless, the taste and bouquet depend very much upon the type of grapes, the soil, degree of ripeness, etc. etc. Pure cultures of the yeasts are always made from types found on the native grapes and in the resulting wines.

Excellent results with pure cultures have been obtained by Wortmann in the manufacture of **sparkling** wines (see **Champagne**), the isolated races producing very little turbidity and depositing as sediment on the cork. A pure culture for the production of sweet wines has been introduced with success by *Seifert*. These cultures are distinguished by their resistance towards a high alcohol and sugar content. Owing to the great variability of wine yeast types and the extreme shortness of the season of wine fermentation, the wine yeasts are not cultivated in large apparatus as in the brewing industry, but only in small quantities in special institutes, *e.g.*, in Germany in the *Staatlichen Versuchsanstalt zu Geisenheim*. The wine manufacturer propagates his yeast in about 12 l. (3 gals.) of pure boiled **must**, and when this is in a vigorous state of fermentation, adds it to the bulk of his **must**. This latter must *not* be previously sterilised by boiling; as a rule, this occasions no inconvenience, for the added yeast develops so rapidly that it overcomes and suppresses not only undesirable wild yeasts, such as *S. apiculatus*, but also equally dangerous bacteria, especially acetic acid bacteria. Pure culture wines also clarify quicker and better than ordinary wines, and the bouquet of the young wine is generally better.

The Principal Period of Fermentation lasts three to fifteen days, and sometimes longer. The fermentation takes place in large casks or butts, the bung of which usually remains open. A little air is required; much air causes the development of acetic acid bacteria and the souring of the wine. The half-fermented wine (and also the **must**) is often consumed locally early in November, especially in the Rhine districts. The fluid in this condition, however, will not keep, and must undergo a further period of fermentation. Consequently as soon as the first vigorous fermentation is over, an "**after-fermentation**" is allowed to take place for several months. If the wine is "white wine," the cask is now filled to the bung with young wine and allowed to stand in the cask in which fermentation has taken place. If the wine is **red**—*i.e.*, if the fermentation has been allowed to proceed in the presence of the grape skins until their colouring matter has partially passed into solution—the wine is at this stage drawn off from the grape skins and run into other casks and loosely bunged.

During this after-fermentation a sediment settles at the bottom and sides of the cask, consisting principally of potassium hydrogen tartrate (tartar) and yeast cells. The tartrate gradually crystallises out of the solution. This residue, called "wine lees," is worked up for tartaric acid (which see).

Storing and Ripening of Wine.—When almost all the sugar in the young wine has fermented into alcohol and carbon dioxide, and the liquid has stood until clear, the young wine is run off into large oaken wine-butts, tightly bunged up, and allowed to "ripen" in a cool cellar. This "ripening" is a very important process, making the wine drinkable, and giving it its characteristic "bouquet" and taste. The wooden walls are porous, and a small amount of oxygen filters in, while at the same time alcohol passes out and evaporates away from the wood. The volume of wine, therefore, slightly diminishes, and an air-space is formed over the liquid in the cask. If the air-space becomes too large it must be filled in,

otherwise fungi will develop. In order to diminish this loss of wine by evaporation attempts have been made to replace the wooden casks by non-porous vessels, made of glass or cement; but such receptacles have always proved quite unsuitable.

The bouquet is now gradually formed out of three different classes of substances: (1) from pleasant smelling and tasting substances originally present in the grape; (2) from similar substances formed during the period of fermentation by the vital activity of the yeast; (3) from wine-fusel oils, which are higher alcohols and by-products of fermentations.

The various alcohols and organic acids present gradually unite during the period of storage, and form pleasant smelling and tasting esters. The wine, however, does not continue to indefinitely improve with storage. It reaches an optimum, and then begins to deteriorate in taste, for the esters continue to increase while the alcohol content diminishes. Very old wine has a decidedly unpleasant, oily, sour taste. The ripening is sometimes accelerated by repeatedly drawing off the wine from one cask into another, and thus aerating it (Racking).

During this period of ripening a turbidity appears in the wine, due to precipitating albuminous substances and yeast cells. Before the wine can be bottled it must be clarified in such a manner that, once bottled, it remains clear. This is achieved by adding "finings," consisting of white of egg, gelatine, isinglass, ox blood, milk, or casein. These substances coagulate, and either sink to the bottom of the vessel, carrying with them all suspended matter, or rise to the surface, and are expelled through the bung hole. A better method of *fining* is to use a soluble sodium compound of *casein* (p. 79), dissolved in 10-20 parts of water. No flavour, precipitation complete.

"Plastering," or the addition of gypsum to the must, is said to improve the colour of red wines; the gypsum combines with part of the water, and increases the relative proportion of alcohol; this retards the fermentation and gives a longer time for the extraction of the colouring matter. Hence the improvement in colour. The calcium sulphate converts the soluble potassium salts into insoluble lime salts and potassium sulphate. Wine thus treated, therefore, not only contains gypsum but also potassium sulphate, and a considerable percentage of sulphates has injurious effects on the human organism. For this reason the addition of gypsum to wine should be condemned.

Diseases of Wine.—Wine is subject to several serious defects or maladies; among these we may mention: (1) The formation of *Mycoderma vini*, which occurs as a growth covering the wine after moderate exposure to the air. It destroys the flavour and renders wine flat. (2) The growth of *Mycoderma aceti*, which turns wine into vinegar. The acetic acid in normal wine should not exceed 0.2 per cent. (3) **Bitterness** due to various mould organisms and bacteria. All red wines are very liable to this disease. (4) The growth of the mould *Oidium vini*, which results in a mousy smell and the destruction of colouring matter. (5) **Ropiness** or **viscidity**, caused by the growth of organisms such as *Pediococcus acidi lactici*, *Bacillus viscoses*, etc. The wine becomes so viscous that it can be drawn out like birdlime. The disease is due to the decomposition of the remaining sugar into mannite and mucilage. It develops in wines deficient in tannin and alcohol. (6) **Foulness**—the development of an unpleasant smell, due to the formation of H_2S, mercaptans, etc. Due to the presence of too much sulphur in the wines; it may be produced by the excessive use of sulphur as an antiseptic, or by an excess of albuminoid matter in the wine. Storage at too high a temperature is a frequent source of disease.

The best means of preventing the deterioration of wine is to preserve the most perfect cleanliness in all processes, apparatus, and vessels. In its initial stages the malady may often be checked by lowering the temperature of storage, or by running the wine into *casks* which have been thoroughly disinfected by burning sulphur in them or by rinsing with a concentrated solution of sodium bisulphite. The addition of other antiseptics, such as **salicylic acid** or **boric acid**, is reprehensive and in many countries illegal. *Pasteur* introduced the process of "**Pasteurisation.**" The bottled wine is heated to 60° C. in special vessels. This kills the injurious fungi and does not harm the wine. A higher temperature than 60° C. destroys the fine taste. In many districts alcohol is added to wine, as a high percentage of alcohol confers stability.

Improving Wines.—Only the very best varieties of wines are consumed unchanged as they come from the wine producer. Almost invariably wines are **blended** or mixed with other wines, chosen in such a way as to neutralise their defects. Thus sour wines are blended with sweet, wines with a poor aroma are blended with wines with a rich fine bouquet, thin wines with full bodied, etc. etc.

The following chemical methods of improving the quality of **wine must** and **wines** are in use:—

(*a*) **Removal of Acidity.**—Excess of acid in a wine is very detrimental to

its flavour. Chaptal's method of reducing acidity is to add pulverised marble or pure calcium carbonate. 60 parts of free acid as a rule require 50 parts of calcium carbonate for neutralisation. If the acidity is due to tartaric and malic acid, the method is very successful, a part of the acid being precipitated as calcium tartrate, and the wine retains only a very small amount of the calcium salt. $CaCO_3$, however, is of no use in the case of acetic acid fermentation, since the calcium acetate formed is soluble and remains in solution.

Sugar of lime (slaked lime + sugar water, decanted from undissolved lime) and neutral potassium tartrate are also used for removing acidity. The latter combines with the tartaric acid to form potassium bitartrate, which settles as an insoluble salt on the sides of the vessel.

According to Gall, a normal **must** should consist of free acid 0.6 per cent., sugar 24 per cent., water 75.4 per cent. The total acid, calculated as tartaric acid, should be within the limits 0.4-1.5 per cent.

(*b*) **Addition of Sugar.**—Many wine **musts** are poor in sugar; this is especially the case in a wet or cloudy season. A good wine **must** should contain 20-24 per cent. of sugar, and when deficient in this it is often the custom to add to the **must** the proper amount of **invert sugar** to bring it up to the standard. The addition of **starch sugar** (glucose) is not suitable, and is illegal in many countries. It has been found that 15 per cent. of sugar in the **must** produces 7.5 per cent. of alcohol in the prepared wine. Consequently the amount of sugar to be added, when the acid is in excess, is 2 parts for each 1 part of additional alcohol required in the finished wine.

(*c*) **The Addition of Alcohol.**—The presence of a high percentage of alcohol in wine makes it stable. For this reason, Madeira, Sherry, Port, etc., before export have usually alcohol, in the form of brandy or spirits, added to them in such a quantity as to raise the alcohol content to over 20 per cent. Although certain wine yeasts are capable of completely fermenting a 30 per cent. must, yet it may be taken as a rule that wines containing more than 15-17 per cent. of alcohol have had alcohol added to them.

From what has been said above it will be seen that the value of a wine *increases* with the amount of alcohol contained in it, and *diminishes*—within certain limits—with the amount of acid.

Chaptal's Method (1800) of improving **wines** and **wine musts** was (*a*) to neutralise the excess of acid with marble (50 marble to every 60 of acid); (*b*) to add sugar to the must in quantity sufficient to render the must normal, and thus restore the amount of alcohol to its proper amount in the finished wine (2 parts of invert sugar for every 1 part of alcohol required).

Gall's Method is to (*a*) reduce the amount of acid by diluting the must with water; (*b*) to add the proper amount of invert sugar to render the **must** normal.

An example will make this clear: Suppose a grape **must** contains 10 per cent. of sugar and 2 per cent. of acid. To make it normal we should require the addition of sugar and water to it in such amount as to reduce the acid to (say) 1 per cent. and increase the sugar to (say) 20 per cent. Since 2 parts of acid are contained in 100 parts of **must**, we should dilute the volume to 200 in order to reduce the percentage of acid in it to 1 per cent. Then 200 parts of the diluted must contain only 10 parts of sugar. Hence to raise the percentage of sugar to 20 per cent., we add to it 30 parts of sugar. The must would then contain 20 per cent. sugar and 1 per cent. acid. It should be noted, however, that in the different countries there are different legal limits to which the dilution may be carried. Thus in Germany water may only be added in quantity sufficient to reduce the **extract** to 1.6 per cent. in the case of **white wine** and 1.7 per cent. in the case of **red wine.**

Petiot's Method is based on the fact that the colouring and bouquet constituents remaining in the grape skins (marc) after the removal of the must are sufficient in amount to impart the colour and flavour of wine to a solution of sugar. The method, in fact, is an attempt to obtain a wine without the aid of **grape juice.** To the pressed grapes (marc) cold water is added in amount equal to the removed **must,** and the whole allowed to mix during two to three days, during which time the water takes up the various soluble constituents of the marc. The liquor is now pressed off, and the amount of sugar and acid it contains is determined. There is usually only 2-3 per cent. of sugar. Consequently an addition of 17-20 per cent. of sugar is made to render the must normal. If there is too little acid, **tartaric acid** is added to approximate to the acid contents of a normal **must.**

The artificial must thus obtained is then fermented in the usual way; while the grape skins are again treated as before, a longer immersion, however, being now made. The resulting wines are usually darker in colour than natural wines, and contain much tannin. They are usually artificially flavoured. Petiot's method is used in France, but is illegal in Germany.

Freezing Wines is employed for the purpose of reducing the aqueous contents, the water freezing out first, leaving an alcohol-rich fluid behind. When wine is cooled to 0.6° C., a precipitate of potassium tartrate, nitrogenous substances, and colouring matter is formed. When this precipitate is removed, the wine, enriched in alcohol, is not liable to after-fermentation, and can be kept in vats and half empty casks.

Scheele adds glycerol (limits 1-3 l. per 1 hl. of wine) to wine.

Different Kinds of Wines

Effervescing Wines—Champagne.—The bulk of champagne comes from France (1903, 35 million bottles; Germany produced in 1904 about 11 million bottles). The method of manufacture is as follows: Only best quality grapes are used, and the juice is expressed as rapidly as possible in order to prevent the wine taking colour from the grape skins. The juice from the second or third pressings is used for making inferior or red-tinted effervescing wines. The expressed juice is allowed to stand twenty-four to thirty-six hours in vats, whereby any earthy matter, etc., is deposited. The juice is then run into the fermenting tanks and allowed to ferment for about fifteen days. It is then put into securely bunged casks, sometimes with the addition of brandy (1 bottle to 100 bottles of juice). At Christmas the wine is fined with isinglass, and again in February. In April the wine is bottled. It should contain 16-18 per cent. sugar, 11-12 per cent. alcohol (by volume), and free acid *equivalent* to 03-05% H_2SO_4. Before bottling it is mixed with 2 per cent. of pure cane sugar in solution and some yeast, securely corked, allowed to ferment again at 24° C., and then allowed to lie horizontally in bins for one to two and a half years. The bottles must be specially strong and without flaw, for the pressure of the CO_2 in them rises to 5-6 atmospheres. Nearly 5 per cent. of the wine is lost by the bursting of the bottles. During the summer a deposit of yeast is gradually formed. In the following winter this is removed by placing the well-cooled bottles mouth downwards in special shaking machines and shaking repeatedly, when the deposit settles on the cork. The cork is opened for a moment, when the yeast is instantly shot out; a quantity of liquor, consisting of a solution of sugar in cognac, is now rapidly added, a new cork inserted and securely wired on. If the wine is still not clear the process must be repeated. The last lot of sugar added does not ferment owing to the absence of yeast. The wine must be perfectly clear. The carbon dioxide is chemically combined in the fluid, and should slowly escape from the cooled wine in small "pearls." The composition of sparkling wines varies widely. The following are typical analyses:—

Parts of Wine Contain.	Sample 1.	Sample 2.
	Per Cent.	Per Cent.
Free acid (counted as H_2SO_4)	0.53	0.78
Alcohol	8.40	9.80
Sugar	4.30	9.10
Extractive matter	7.50	15.20
Specific gravity	1.029	1.041

All wines are capable of being produced as effervescing wines if the bottling is performed before the fermentation is over; for the carbonic acid is retained in the wine, and, on opening, the rapid disengagement of gas causes effervescence. Not only genuine champagnes, but also Hocks, Moselles, and red wines, may be thus treated with good results. If the wine contains much sugar, the fermentation is

arrested in the bottle before all the sugar is consumed, and the result is a sweet effervescing wine. If, however, the sugar is all exhausted in producing CO_2 and alcohol, **dry** effervescing wine is produced. Dry effervescing wines usually agree better with the digestion than sweet wines.

Cheap imitation champagnes and sparkling wines are now manufactured by pumping in CO_2 under pressure. They usually become turbid on keeping, and the CO_2 in them is not so stably bound as in genuine champagnes.

Most **Sweet Wines, Dessert Wines,** and **Medicinal Wines** are *artificial products*. In other words, they are not obtained by the natural process of fermentation of fresh grapes, but more or less alcohol or sugar is added. The best-known types of sweet wines are: **Tokay, Port, Sherry, Madeira, Malaga,** etc.

Tokay is obtained from ripe grapes which have been allowed to partially dry, either on the vine tree itself, or on **straw** after plucking, so that the sugar is unable to completely ferment.

Port Wine is obtained by fermenting the must down to 6-8 per cent. of sugar, and then 4-7 per cent. of alcohol is added to arrest further fermentation. The wine then contains 14-15 per cent. of alcohol. In the spring the wine is racked, and 2-3 per cent. more alcohol added. The final product contains 20-24 per cent. of alcohol. By suitable "blending," the best results are obtained.

Sherry Wine is made from several varieties of white grapes of Andalusia, Spain. After each pressing of the grapes the wine is "plastered" with gypsum. The must is fermented to 8-10 per cent. sugar, and alcohol is added to bring the percentage up to 16-18 per cent. Sherry wine is usually ripened by "baking" the wine by natural or artificial heat. The filled wine casks are placed in tiers in a building with roof and side of glass. The temperature in the sherry house is as high as 60° C., and at night time is maintained by fires.

Different Kinds of Wines.—The following is a list of the best-known wines, arranged according to the country of production:—

1. **French Wines.**—Barsac, Burgundy, Chablis, Champagne, Claret, Frontignac (Muscat), Graves, Hermitage, Medoc, Roussillon, Saumur, Sauternes, etc.
2. **German Wines.**—Riesling, "Rhine," "Moselle," and "Pfalz" are applied to wines made in the respective districts. "Hock" is also the name of certain Rhine wines.
3. **Italian Wines.**—Asti, Barbera, Barolo, Capri, Chianti, Falerno, Lacryma Christi, Marsala, Muscat of Syracuse, Nebbiolo, Valtellina, etc.
4. **Austria-Hungarian.**—Ausbruch, Goldeck, Tokay, Vöslauer.
5. **Spanish.**—Malaga, Sherry, Val de Penas, Vinos Tintos.
6. **Portuguese.**—Carcavellos, Collares, Lisbon, Ports.
7. **Madeira and Canary Islands.**—Canary (sack), Madeira, Malmseys, Malvasia.
8. **Swiss.**—Gringet, Montreux, Neuchâtel.
9. **Greek.**—Corinth, Hymettus, Kephisia, Noussa, Patras, Santorin, etc.
10. **Turkish.**—Candian (Crete), Cyprus, Mt. Lebanon, etc.
11. **Russian.**—Crimean, Donski, Kakhetian (Caucasus), Krimshi.
12. **Persian.**—Shiraz.
13. **Australian.**—Australian Burgundy, Hermitage, Port, Sauterne, etc.
14. **South African.**—Cape Madeira, Constantia.
15. **American.**—Californian Port, Champagne, etc.

Alcoholic Strengths of Wines.—These vary somewhat. The following numbers are typical:—

	Specific Gravity.	Alcohol per Cent. by Volume.		Specific Gravity.	Alcohol per Cent. by Volume.
Burgundy -	0.9913	10.5	Port (natural) - -	0.9992	14.5
Champagne -	1.0109	10.4	„ (fortified) - -	....	21.5
Claret - -	0.9950	9.6	Rhine - - -	0.9928	10.2
Marsala - -	0.9959	16.0	Sherry - - -	0.9859	16.0

Wine Production of the World.—The following figures show the quantity of wine produced by the leading wine-producing countries of the world for the year 1909.

VINTAGE FOR 1908 AND 1909

Country.	Hectolitres.	Hectolitres.*	Country.	Hectolitres.	Hectolitres.*
	1908.	1909.		1908.	1909.
France	60,545,265	54,445,863	Russia	2,800,000	2,400,000
Italy	47,868,000	41,398,000	Germany	3,135,953	1,900,000
Spain	18,556,717	14,767,911	Greece	2,800,000	2,200,000
Algeria	7,803,734	8,228,719	Turkey and Cyprus	1,800,000	1,500,000
Austria	8,399,964	4,500,000	Argentine	1,250,000	1,100,000
Portugal	3,900,000	3,100,000	United States	1,197,951	1,500,000
Hungary and neighbouring lands	5,500,000	1,925,000	Switzerland	1,200,000	1,010,000

* 1 hectolitre = 1,000 litres = 220.4 gallons.

The English *import* of wine in 1910 reached 13,735,000 gals., value £4,249,000. The *export* was 798,000 galls., value £468,000. The United States in 1910 imported $6,300,000 champagne and $6,605,000 still wines. The export was $225,000. California produced 130,000,000 gals.; State of New York, 22,000,000 gals.; Ohio, 17,600,000 gals. Invested capital, $100,000,000. For statistics regarding **Mineral Waters, Fruit Wines**, etc., see p. 250.

FRUIT WINES, ETC.

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DE BOUTTEVILLE ET HAUCHECORNE.—"Le Cidre." Rouen, 1875.
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DOCHNAHL.—"Künstliche Weinbereitung." Basel, 1895.

Wine is usually prepared from grape juice merely because it is the richest in sugar, contains pleasant-tasting organic acids, and the fermentation is easy to carry out; moreover, the product is very stable. Nevertheless the juices of other fruits, such as apples, pears, gooseberries, currants, elderberry, figs, rhubarb, etc., can also be fermented, and if sugar is added to the juice until it contains about 20 per cent., excellent wines may be obtained. Sometimes nitrogenous food stuffs must be added to the juice to cause the yeast to properly grow.

In **Germany, France,** and **England** a considerable amount of **cider** ("apple-wine") is produced by the fermentation of apple juice. France produces nearly 20,000,000 hl. of cider yearly. Cider is distinguished from grape wine by the absence of tartaric and citric acids. It may contain 5-6 per cent. of alcohol. If a moderate proportion of tartaric acid is added to cider the product cannot be distinguished from wine. In gooseberry, currant, and other fruit wines tartaric and citric acids are usually absent.

Palm Wine is fermented juice of the sugar palm, and is largely consumed in tropical countries.

Saké is an alcoholic drink made from rice by the Japanese and Chinese. The rice is saccharified by means of the mould *Aspergillus oryzæ* (see pp. 226, 286), and the liquid fermented by another yeast mould called "Mots." Saké contains 10-15 per cent. of alcohol and little extract or CO_2.

Aerated and Mineral Waters (Artificial) are made by forcing carbonic acid gas into water (best distilled) in which various salts and flavouring matters are dissolved. Saturation with CO_2 is usually carried out under 5 atmospheres pressure, the CO_2 being now usually supplied in a liquid form in steel cylinders. At one time—and to some extent at present—special apparatus were employed

in which the CO_2 was generated, the generators being usually of copper internally coated with lead or earthenware, and the CO_2 was obtained by the aid of HCl or H_2SO_4 on marble, chalk, magnesite, etc. The gas is always purified by passing through (*a*) water, (*b*) NaOH, (*c*) $FeSO_4$ and $NaHCO_3$ (to remove H_2S), (*d*) $KMnO_4$. For the apparatus employed see the special works below referred to.

Lemonades contain sugar, citric, or tartaric acid and sometimes scents. Ordinary "**Seltzers**" consists of cryst. Na_2CO_3 (25) + NaCl (5) + Na_2SO_4 (cryst.) (6) + 10,000 H_2O. **Apollinaris** = 217 $NaHCO_3$ + 4.5 NaCl + 2.8 Na_2SiO_3 + 29 $CaCl_2$ + 42.8 $MgCO_3$ + 16.7 $MgSO_4$ + 3 $FeSO_4.7H_2O$ + 1.7 HCl, all dissolved in 100,000 water.

The finished waters usually contain CO_2 under a pressure of 1½-2 atmospheres.

Literature.—SULZ, "Beverages" (New York, 1888); KIRKBY, "Artificial Mineral Waters" (Manchester, 1902); TENIM, "Limonaden u. alkoholfrein getranke" (Vienna and Leipzig, 1909); FRITSCH, "Eaux et Boissons gazeuses" (Paris, 1906); HIRSCH-SIEDLER, "Künstlichen Mineralwâsser" (Braunschweig, 1897); HERMANN-LACHAKELLE, "Boissons gazeuses" (Paris, 1891); GOOLD, "Aerated Waters" (London, 1881).

Statistics.—England *imported* in 1910: Aerated and mineral waters, 1,694,000 dozen bottles, value £341,000; cider and perry (sugar free), 261,000 gals., value £8,000; wine, 13,735,000 gals., value £4,249,000.

The *export* in 1910 was: Aerated and mineral waters, 1,438,000 dozen bottles, value £235,000; wine, 798,000 gals., value £468,000. The United States in 1910 imported: cherry juice and other fruit juice, 38,000 gals. (value $27,000); prune juice, 24,000 gals. (value $18,000); cider, 8,000 gals. (value $8,000); lemonade and soda water, 66,000 doz. pints (value $55,000). The United States export of cider sank from 344,000 gals. (value $54,000) in 1906 to 6,000 gals. (value $2,000) in 1910. The export of fruit juice was $52,000 in 1906 and $85,000 in 1910. Only $2,000 of mineral waters were exported in 1910.

Chemical Analysis of Wine

For details readers should consult the special works mentioned above, especially the article on "Wines and Potable Spirits" in Allen's "Commercial Analysis," vol. i. (1909). The following is a summary of the methods employed:—

1. **Alcohol Percentage.**—The natural wines contain 7-12 per cent., seldom over 15 per cent. Certain Spanish and Portuguese export wines, *e.g.*, Port, contain 20-23 per cent. ("Fortified" wines). The alcohol is determined by distillation. 50 c.c. of wine are mixed with 25 c.c. of water and distilled until 50 c.c. of fluid has passed over. The alcohol is determined in the distillate by taking its specific gravity by means of the Pyknometer (15° C.), and then using special tables (*e.g.*, Windesch's).

2. **Extract** is the substance which remains behind on evaporating the wine to dryness on the water bath. In natural wines it amounts to 1.8-2.5 per cent., and should never be less than 1.6 per cent. It is determined by evaporating 25 or 50 c.c. of wine to dryness, first to a syrup on the water bath and then for two hours in the steam oven. Also from the specific gravity of the original wine and of the alcoholic distillate. If S = specific gravity of the wine, and S′ = specific gravity of alcoholic distillate (see 1), then percentage extract (in grams per 100 c.c.) = (S − S′) ÷ 0.00386.

3. **Sugar.**—Ordinary dry wines contain very little sugar, but sweet wines often contain several per cent., usually as **invert** sugar. The amount of **invert sugar** is obtained in the usual way by Fehling's solution, the wine being first neutralised with NaOH and decolourised by basic lead acetate solution. The **cane sugar** is determined by hydrolysing 50 c.c. of the clarified and neutralised wine with HCl, and then estimating by Fehling's solution. The total titration, less than that due to the invert sugar, gives the amount of cane sugar. The amount of impure starch sugar (which is accompanied by dextro-rotatory non-fermentable dextrine) is found by fermenting it and taking the specific rotation. For details see Allen's "Commercial Analysis."

4. **Free Acids.**—Reckoned as free tartaric acid, the total free acids usually amount to 0.4-1.0 per cent. of the wine. In France it is customary to calculate the acidity as equal to so many grams of sulphuric acid per 1,000 c.c. To determine the acidity the hot liquid is rapidly titrated with $\frac{N}{2}$ NaOH, using litmus paper as indicator. The **Volatile acids**, which, counted as acetic acid, amount to 0.1-0.2 per cent., is determined by distilling 50 c.c. of the wine in a current of steam free from CO_2 and titrating with $\frac{N}{10}$ NaOH, using phenolphthalein as indicator. The total amount of tartaric acid present is found by precipitating with potassium acetate and alcohol.

5. **Mineral Salts.**—Wines seldom contain less than 0.15 per cent. of mineral salts. Wines on the average contain about 0.1 per cent. of K_2SO_4. More than 0.2 per cent. is held to be evidence of "plastering," *i.e.*, the addition of gypsum to the must. In Germany and France wines containing more than 0.2 per cent K_2SO_4=0.092 per cent. SO_3 are *illegal*. In France wines must not contain more than 0.1 per cent. NaCl.

6. **Sulphurous Acid** must not in France and Switzerland exceed 200 mg. per 1,000 c.c. Free sulphurous acid must not exceed 30-20 mg. per 1,000 c.c.

7. **Glycerol** lies, usually, between 0.4 and 1 per cent., sometimes 0.16-1.4 per cent.

8. **Foreign Colouring Matters.**—Coal-tar colours are usually detected by boiling cleaned wool (previously mordanted with alum and sodium acetate) with wine. The foreign colours are precipitated on the wool and are examined by the usual reagents. Coal-tar colours are also detected by the **lead acetate** test (see Allen), by Cazeneuve's mercuric oxide test, by extracting with ether before and after supersaturation with ammonia, and by extracting with amyl alcohol. The artificial addition of bilberry or other fruit juices—which contain natural colouring matters very similar to that in grape skins—is, however, very difficult to detect.

Brandies from Wine.—These are obtained either by directly distilling the marc (fermented grape skins) or second wines derived from it. The best kinds of brandy, "cognacs," are obtained by distilling good wine. The wash for brandy spirits is obtained by running water into a tank filled with the mash, the overflow running into other similar tanks. The fluid is distilled when it contains over 5 per cent. alcohol. See under **Spirit Manufacture.**

Wine Fusel Oils vary very much in composition, according to the nature of the must, their fermentation and storage. They occur in wines, but also, and to a far larger extent, in genuine cognacs (obtained by distilling wine). Of the following samples the first was obtained by distilling an old cognac, while the second was obtained from the fermentation of a cane sugar solution with wine yeasts:—

COMPOSITION OF WINE FUSEL OILS (after *Ost*)

1. IN 100 L. COGNAC.		2. FROM 100,000 G. CANE SUGAR.	
Normal butyl alcohol	218.6 g.	Alcohol	50,600 g.
Amyl alcohol	83.8 ,,	Glycerol	2,100 ,,
Normal propyl alcohol	40.0 ,,	Succinic acid	452 ,,
Ethyl acetate	35.0 ,,	Acetic acid	205 ,,
Acetal	35.0 ,,	Isobutylene glycol	158 ,,
Esters of fatty acids	7.0 ,,	Amyl alcohol	51 ,,
Acetaldehyde	3.0 ,,	Normal propyl alcohol	2 ,,
Heptyl alcohol	1.5 ,,	Isobutyl alcohol	1.5 g.
Hexyl alcohol	0.5 ,,	Esters of organic acids	2.0 ,,
Amine bases	4.0 ,,		

The wine fusel oils are either obtained by the fractional distillation of fermented grape skins or wine lees (marc), when they are known as "cognac oil," or "grape oil." They are sometimes artificially made for adding to brandies and cognacs (see p. 384). It will be noticed that they are entirely different in character to the fusel oils obtained from whisky or potato spirit manufacture (see under **Spirits**, pp. 312, 298).

IV.—BEER

By C. H. Griffiths and G. Martin, Ph.D., M.Sc.

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Beer is an alcoholic beverage obtained from malt, hops, and water. It differs from wine and spirits in containing less alcohol (3-6 per cent.) and being richer in extracts (4-8 per cent.).

Statistics Relating to Beer.—The following numbers show the production of beer in the principal countries of the world, and also the amount of beer consumed per head of the population. It will be seen that the United States is now the greatest beer-producing nation (*Ost*):—

Country.	Production in Millions of Hectolitres.*	Consumption per Head of the Population in Litres.
United States (1909)	66.0	79
Germany (1909)	64.8	100
England and Ireland (1907)	58.3	126
Austria (1908)	20.4	73
Belgium (1908)	14.0	210
France (1905)	13.7	35
Russia (1904)	6.2	5
Italy (1905)	0.24	1

* 1 hectolitre = 100 litres = 22.01 gallons; 1 barrel = 36 gallons.

In 1908-09 in the *United Kingdom* there were 4,667 breweries; these produced 34,953,274 barrels. The duty levied on each barrel of beer was 7s. 9d., the total revenue raised being £13,144,445.
The amount of material used in 1908 for brewing in the United Kingdom was:—

Malt, 50,960,923 bushels.
Unmalted corn, 91,069 bushels.
Rice, maize, flaked rice, etc., 1,278,988 cwt.
Sugar, including its equivalent of syrup, glucose, and saccharum, 2,883,269 cwt.
Hops, 62,971,755 lbs.
Hop substitutes, 4,479 lbs.

In Germany (*Norddeutschen Brausteuergebiete*) during 1909 the following quantities of raw products were used in brewing 38.4 million hectolitres of beer:—

Barley malt	6,650,000 dz.*
Wheat malt	94,200 ,,
Rice (raw)	83,300 ,,
Sugar and (little) syrup and other malt substitutes	47,200 ,,

The largest German brewery (Schultheiss) used in 1909 no less than 240,000 dz.* malz.

Within recent years small firms have been steadily diminishing and large ones increasing. In 1874 there were in the United Kingdom no less than 34,000 breweries, whereas now the number is 4,667. The largest English breweries are: Guinness & Co., Dublin (capital £7,000,000; over 2,000,000 barrels), Bass, and Allsopp, in Burton-on-Trent (the first having a yearly output of between one and two million barrels). In 1899 the amount of capital invested in breweries in the United Kingdom was over £240,000,000.

On the Continent the largest breweries are: Dreher in Kl. Schwechat-Wien, Schultheiss in Berlin (1,000,000 hl.). München yields 3,000,000 hl.; the largest brewery in the town being the Löwenbrau (320,000 barrels). In Northern Germany, each hectolitre (100 l. = 22.01 galls.) has to pay a duty of 2.4 m. (1909), and in Bayern, 4.8 m. The total revenue derived from this beer duty for the whole German Empire was in 1909 154,000,000 m. [20 m. = £1].

The capital invested in the American brewing industry in 1909 was $671,158,000, being an increase of 30 per cent. in five years. The value of products was $374,730,000 in 1909. The number of breweries was 14,100. The average capital per establishment was $475,000 in 1909 against $337,000 in 1904. 223 breweries in 1910-11 were equipped with pipe lines for conveying beer to the bottling premises. The duty paid for ale, beer, lager beer, porter, etc., for 1910-11 was $63,216,851. The total production of malt liquors in 1910-11 was 63,283,000 barrels, against 40,517,000 barrels in 1901-02.

Outline of the Theory of Brewing.—Most corn grains consist of about 60-65 per cent. of starch, a complex hydrocarbon of the constitution $(C_{12}H_{20}O_{10})_{20}$ (Brown and Morris). Starch, however, will not undergo alcoholic fermentation. It must first be broken down into simpler carbohydrates. This is achieved by allowing the *grain to germinate* (malting). During the process of malting the enzyme **diastase** is formed. This is capable of attacking the starch, breaking it down into the sugar **maltose**, $C_{12}H_{22}O_{11}$, and into dextrin $(C_{12}H_{20}O_{10})_{20}$. The diastase is soluble in water, and acts best between 40°-60° C. Consequently the germinated grain (malt) is crushed or ground and mixed with hot water ("mashed") in order to let the diastase act freely on the starch. This it does, the bulk of the starch being rapidly converted into maltose. The solution is now boiled to destroy the diastase, and yeast is added. This, and also malt, contains an enzyme called **maltase** which rapidly decomposes the maltose, $C_{12}H_{22}O_{11}$, into 2 molecules of the simpler sugar, dextrose, $C_6H_{12}O_6$: $(C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6)$; then another enzyme contained in the yeast, Buchner's "Zymase," rapidly converts the dextrose into alcohol and carbon dioxide: $(C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2)$. The resultant beverage is known as beer.

The grain used for conversion into malt is barley. Sometimes, however, other sorts of grain are mixed with the malt in the mashing process, the diastase of the malt being able to attack their starch.

From this short description it will be seen that the manufacture of beer naturally resolves itself into three distinct processes:—

1. The preparation of malt, *i.e.*, germinated barley.

2. The preparation of the wort, or fluid which is to be fermented. This stage of manufacture may be further divided into (*a*) the mashing process, or the mixing of the ground malt with hot water and its saccharification; (*b*) boiling and hopping the wort to destroy the diastase; (*c*) cooling the wort.

3. Fermentation of the wort and storage of the resulting beer. Each of these processes will now be described in detail.

THE PRODUCTION OF MALT

Raw Materials used in Brewing.—Barley is the grain mostly used for making malt for lager beer, ale, stout, vinegar, and yeast makers' or distillers' mash, while wheat malt is used in Germany and U.S.A. in the production of Weiss-bier.

* 1 dz. = 100 kg. = about $\frac{1}{10}$ ton.

Commercial cultivated barley belongs to the genus *Hordeum*, and species *Hordeum sativum*. Four leading types or sub-species of barley are met with in commerce, viz.: *—

1. *Hordeum distichum.*—These are *two-rowed barleys*, with a *narrow ear* and a comparatively long distance between the corns. Well-known varieties are: Chevalier, Kinver, Archer, Hallett, Hanna, Black and White Ocichæ.

2. *Hordeum zeocriton.*—These are *two-rowed barleys*, with a *wide ear* and a comparatively *short* distance between the corns. *Varieties:* Goldthorpe, Peacock, or Fan Barley. Standwell and Invincible are hybrids resembling Goldthorpe.

3. *Hordeum vulgare.*—These are *six-rowed barleys*, with *narrow ear* and a comparatively long distance between the corns. *Varieties:* Scottish "bere" or "bigg." Most "Light Foreign" six-rowed barleys are mixtures of white and blue *H. vulgare.*

4. *Hordeum hexastichum.*—These are *six-rowed barleys* with *wide ear* and short distance between the corns. *Varieties:* Chilian six-rowed barley is a mixture of white and blue *H. hexastichum.*

Other Raw Materials.—In Germany, as a rule, only malt is used for brewing. In America, however, and to a lesser extent in England, a considerable quantity of raw grain is mixed with the malt, especially maize or rice. Since the malt is very rich in diastase there is enough diastase present not only to saccharify the starch in the malt, but also that in the added raw grain. In Germany sometimes **rice** is mixed with the malt in making top-fermentation beer. The beer thus produced acquires a peculiar taste, and loses in stability.

In England and America, and to a small extent in Germany for special kinds of top-fermentation beer, various kinds of sugar, especially cane sugar, starch sugar (glucose), syrups, etc., are added to the malt. The complete fermentation of the pure sugars increase the amount of alcohol in the beer, leaving unaltered the amount of extract. Starch sugar and syrups, however, which contain non-fermentable isomaltose and dextrine, enrich the beer in extract. **Hops** are added to the beer to give it a bitter flavour and preserve it. The world's production of hops amounts to about 1,000,000 cwt. yearly, England importing about 200,000 cwt. (value about £800,000). The U.S.A. import in 1910 amounted to 3,200,000 lbs. (value $1,500,000), while the export was 10,600,000 lbs. (value $2,000,000). The hops used in brewing consist of the ripe female flowers of the *Humulus lupulus.*

The sticky yellow dust, known as "hop-flour" or "lupulin," attached to the lower inside base of the bracts of the hop cone, contains the resins, volatile oils, and bitter substances which are of value to the brewer. Hence hops are valued by their content of **lupulin** (hop flour), which may amount to 10-15 per cent. of the hops. The resins are acid in nature (lupulin acid, hop bitter acid), very soluble in ether, partly soluble in petroleum, and very sparingly soluble in water. They are divided into α-, β-, and γ- resins, the first two resins being known as "soft resins," and contain the bitter and antiseptic substances which destroy bacteria, which otherwise easily multiply in unhopped beer.

The pleasant aroma given to beer by the hops is due to a volatile essential oil ("Hop oil"), amounting to 0.2-0.8 per cent. in good hops, and consisting of terpenes, $C_{10}H_{16}$, valeral, $C_4H_9.CHO$, etc. etc. Hops on keeping lose their pleasant aroma owing to the conversion of the valeral into valeric acid, $C_4H_9.COOH$. The **tannin** in the leaves of the hops is valuable in that it precipitates albumen and hence helps to clear the wort.

Hops are rendered preservable by drying in kilns and treating with SO_2 fumes (sulphur being thrown on the fire of the drying kiln) and packed in sacks or zinc boxes in a cool place.

Testing the Barley Grain.—The barley, as bought in the open market, should be dry, heavy (55-56 lbs. to the bushel), even in size, pale yellow in colour, sweet in smell, with a thin skin. It should be rich in starch but poor in nitrogen, free from broken grains, free from bacteria and moulds. It should be as free as possible from steely grains and have a good germinative power. The percentage of "steely grains" is usually determined by a simple instrument called a "**Farinator.**' The corns to be tested are placed in a tray containing fifty holes; a slight shake fills each hole with

* See E. S. Beaven, "Varieties of Barley," *Journal of the Institute of Brewing*, 1902, viii. 547.

a grain; they are then cut with the knife crosswise, the result showing in a bottom tray containing fifty corns, so that the percentage of steely grains is easily counted.

The germinating power of the barley is usually tested by means of Coldewe's germinating apparatus, which consists of a glass half filled with water, above it the barley in the porcelain tray filled up with sand and covered with felt, above this is a wooden cover and the attached thermometer forms a handle. It is left in a warm cupboard or any convenient place, and in about ten hours the good grain will have sprouted. The tray holds exactly 100 corns, so that the percentage of idlers is seen at a glance (Fig. 97).

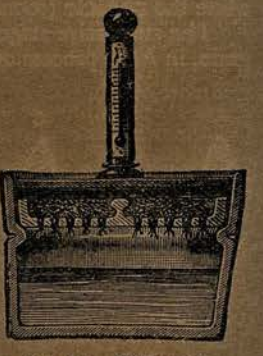

FIG. 97.—Coldewe's Germinating Apparatus.

Should, in a particular sample, anything but an extremely small percentage (2-3) of the grains be incapable of germinating, good malt cannot be made from it. All ungerminated grains form breeding-grounds for mould during the malting process, and represent so much raw barley in the finished malt.

Anatomy and Chemical Composition of the Barley Grain.—The barley grain is very similar in structure to the wheat grain (Fig. 68, p. 179), consisting of two main parts:—

A (Fig. 98), the **Endosperm**, which consists principally of starch cells, surrounded by a husk *a*.

B, the **Germ**, from which the living plant develops.

Between A and B lies a cellulose membrane, *gg*, called the **scutellum**.

c is the **Plumule** or acrospire, *i.e.*, the part which, growing upwards, ultimately develops into the stalk and leaves of a new plant.

d is the radix or **Radicle**, *i.e.*, the part which, growing downwards, develops into the roots of the new plant.

The barley grain consists of 60-65 per cent. starch, which is contained in A, 12-18 per cent. moisture, 8-15 per cent. nitrogenous matter (principally in B), 7 per cent. cellulose and pentosane, 2.5 per cent. fat, 2.5 per cent. ash (very rich in P_2O_5 and K_2O).

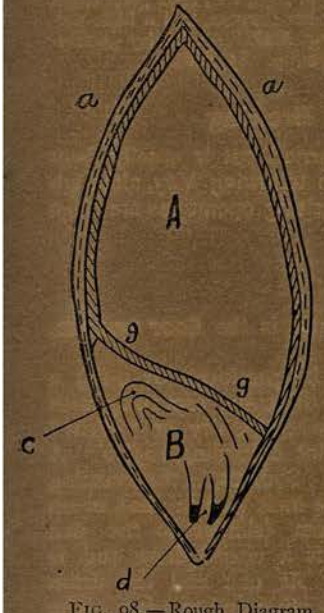

FIG. 98.—Rough Diagram of Longitudinal Section through a Barleycorn. (For greater detail see Section through a Wheat Grain, Fig. 68, p. 179.)

Malting

Theory of Malting.—When barley is moistened and kept at 10°-18° C. for some hours it begins to germinate. When this occurs, Messrs Brown, Morris, and O'Sullivan have shown the enzymes diastase and cytase are producing in considerable quantity in the developing germ B (Fig. 98). The **cytase** dissolves the cellulose membrane *gg* which divides the starchy matter in the endosperm A from the germ B. The diastase can then gradually diffuse from *gg* into the starch in A. The diastase then breaks down the starch into various sugars, principally maltose, but also sucrose and invert sugar is produced. At the same time proteolytic enzymes, such as peptase, appear in the germ B, which hydrolyse the albumens first into peptones and later into amido acids. It is obvious, therefore, that with the process of germination a succession of very complex substances are formed by the developing germ. The germ breathes, absorbing oxygen (hence the practice of aerating malt) and throwing out CO_2 and water, and generates warmth. The great mass of starch contained in the endosperm is, however, quite unaffected by the diastase and other enzymes, on account of the slowness of diffusion. In consequence, however, of the cellulose-dissolving action of the cytase enzyme the cell membranes become loose, and the barley grain becomes soft and is easily gelatinised by boiling water.

Brown and Morris have shown that the formation of diastase takes place principally in the epithelium (the fine membranous lining of the internal organs of the grain), and is favoured by the presence of small quantities of acid, but is almost completely restricted by readily assimilable sugars. Thus if barley be germinated in such a way that a sufficient quantity of cane sugar for the sustenance

of the embryo is always present, no diastase is formed, and it is therefore probable that the diastatic secretion of the epithelium is due to the stimulus of a starvation process.

Growth of the Acrospire and Radicle.—After moistening the grain or "steeping" for forty-eight hours, the **acrospire** grows upwards *under* the skin, while the **radicle** (roots) grows downwards.

The successive stages of growth are represented in the figure. *a* is the original grain, in *b* the process of germination is beginning, in *c* the roots are well developed, and the acrospire has grown nearly half way up the grain. After about seven to eight days the acrospire will be three-quarters way up the grain, and the roots one to one and a half times the length of the corn. This is shown in *d*. When this stage is reached, the process of germination is stopped by heating on kilns.

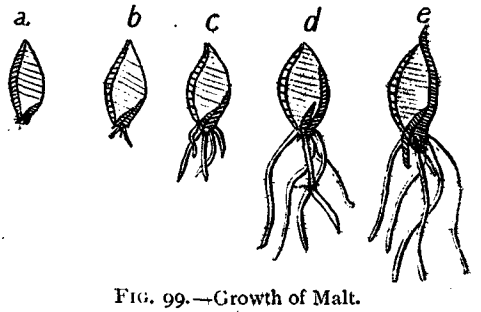

FIG. 99.—Growth of Malt.

The malt should never (in malting for beer) be allowed to germinate so long that the acrospire begins to emerge from under the skin at the top of the grain as shown in *c*. It is true that the amount of diastase increases with growth beyond *d* up to a certain limit, but a growth beyond *d* causes the unnecessary destruction of much starch, and so is uneconomical. Consequently the brewer always works with "short malt" as the product is called. It should be noticed that a fairly low temperature favours the production of diastase, and is necessary for a good brewing malt. Moreover, the brewer always uses **Short Malt** (see p. 285), *i.e.*, malt germinated for a seven to ten day period, which contains sufficient diastase for his purpose, and a high percentage of starch. The *distiller*, on the contrary, works with "**Long Malt**," *i.e.*, barley germinated for twenty days or so, for reasons that are explained under **Spirits** (pp. 285, 286).

Practice of Malting in Relation to Brewing

In England the seasons during which malting is carried out is usually from about the middle of September until the middle of the following May, although where large quantities of foreign barley are dealt with, malting operations are often carried on throughout the whole year.

Floor System of Malting

The system of malting most generally used in England is the **floor system**, which we will now describe:—

Sweating the Barley.—The best malt can only be produced by using a properly dried barley. This is often a matter of great difficulty, especially with English barleys and a wet harvest. Most maltsters, therefore, dry or "sweat" their barley before storing, in **kilns** at a temperature not exceeding 105° F. A space of 16 ft. per quarter is usually allowed in a kiln. Sometimes the sweating is done on the malt kilns between the stages of curing the malt (see p. 260), or on a specially built kiln, or by means of a drying drum (similar to the one shown for germinating barley, Fig. 107). This latter is a closed drum and is rotated by means of a worm and worm-wheel gear. At one end the drum is connected by means of a pipe to a furnace, and at the other end to a fan. The barley is put into the drum by doors in the walls or shell of same. The doors are then closed, the drum set in motion, and hot air from the furnace is sucked through the barley by the fan, which discharges its moisture-laden air into the atmosphere. The exact method to be employed in thus sweating the barley is a matter depending to a great extent upon local conditions.

The sweating process mellows the barley and gets rid of excess of moisture, thus inducing a more uniform absorption of moisture in steeping. Sweated barley should not be steeped within a fortnight of sweating. It does not heat in bins.

Cleaning and Grading the Barley.—The barley is next passed through a rough cleaning machine so as to remove the coarse impurities it contains by means of sieves and blower fans. Then it is sorted out by special "grading" machines into grains of different sizes, which must be steeped separately; for if the grains are of different sizes they will germinate at different rates, and one set of grains will be ready for curing before other sized grains have attained the proper condition. Also, all broken and half corns must be removed, for if such half corns are allowed to get on to the growing floor, they set up mould and create a lot of trouble, often damaging a whole piece of malt.

The Rougher Out may be made either in the form of wire sieves or a rotary wire cylinder enclosed in a wood or iron frame, and having an efficient fan to extract dust and light straws from the machine while in work. An advantage of the machines with sieves is that they are more easy to clean, and the exhausting arrangements are more efficient.

The barley cleaning machine for finishing is very similar in outward appearance to the Rougher Out, but has additional sieves for taking out very thin barley (which is fit only for chicken food), heavy sand, etc. This machine again has a powerful exhausting fan operating over the whole surfaces.

After the barley leaves this machine it passes into half corn separators, which are made from plates of a special metal having indentations (not holes) drilled at regular distances all over their surface. The plates are then rolled into cylindrical form, mounted on a spindle and carried in a wood or iron frame with a slight slope from feed end to delivery end. The cylinders are rotated by means of pulleys and belt; or by bevil gears. The barley is fed into the cylinder, and finds its way into the indentations. The whole corns project for about a third of their length beyond the surface of the plates, and as the cylinder rotates they come into contact with the edge of a tray mounted on the spindle. Contact with this tray has the effect of knocking the whole corns back into the bottom of the cylinder, while the half corns, not projecting in the same manner, are carried beyond the edge of the tray until compelled by gravity to fall into the tray, which is fitted with a worm carrying the half corns out at the end, the whole corns also being carried by the slope of cylinder and the pressure of incoming barley to the end where they are delivered from the machine by a different exit. The whole corns, which of course comprise the thoroughly cleaned barley, should be put into bins reserved for this purpose either directly over the steeping cisterns or so as to command them easily.

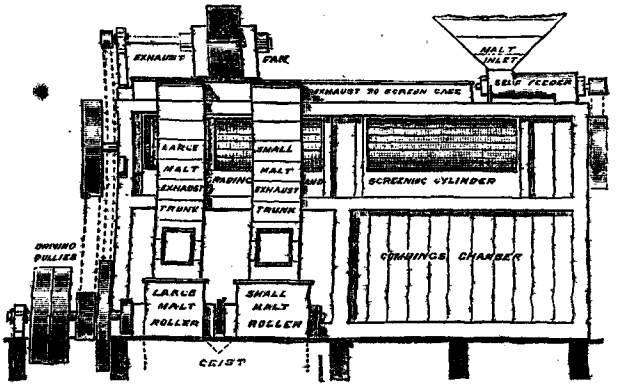

FIG. 100.—Machine for Cleaning and Grading Barley, Malt, and other Grain.
(Llewellins & James, Bristol.)

Dust Control.—In the case of both Rougher Out and Barley Dresser, it is necessary that means should be employed to effectually deal with the dust from the exhaust fans. The old-fashioned way of doing this was to allow the fan to blow into a chamber called a dust chamber or stive room. This chamber had an outlet for the spent air to escape to the open, while the dust was precipitated on to the floor, from which it was afterwards taken away in sacks. This system had many objections, as frequently a large amount of dust was thrown out on to the roof and found its way to the working floors, which was very bad, owing to the presence of various germs. The better way is to allow the fans to discharge into a dust collector, preferably of the dry type, a very good one being that Ilus-

trated in Fig. 101 which consists of an upper and lower box, connected together by a number of tubes; the air escaping through the fabric, the dust being retained, and settling down to the lower box where it is caught in a worm and delivered to sacks on the floor beneath. In order that the pores may not become clogged, a cleaning attachment travels continuously up and down the tubes. The apparatus is extremely effective in work.

Steeping the Barley.—The cleaned and graded barley is now conveyed to the steeping cisterns, and moistened with water in order to start process of germination.

The cisterns for steeping should be made of cast iron with conical bottom in order to be self-emptying. Sparges should be fitted round the four sides at top and an overflow trough with a grid to retain floating corns on one of the top side plates. A very good adjunct to a steeping cistern is a

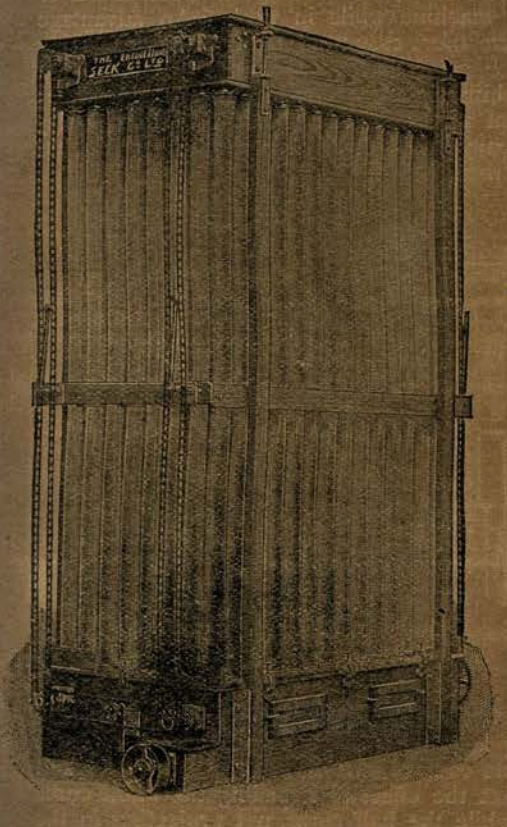

FIG. 101.—Dust Collecting Machine.
(Seck Engineering Co., London.)

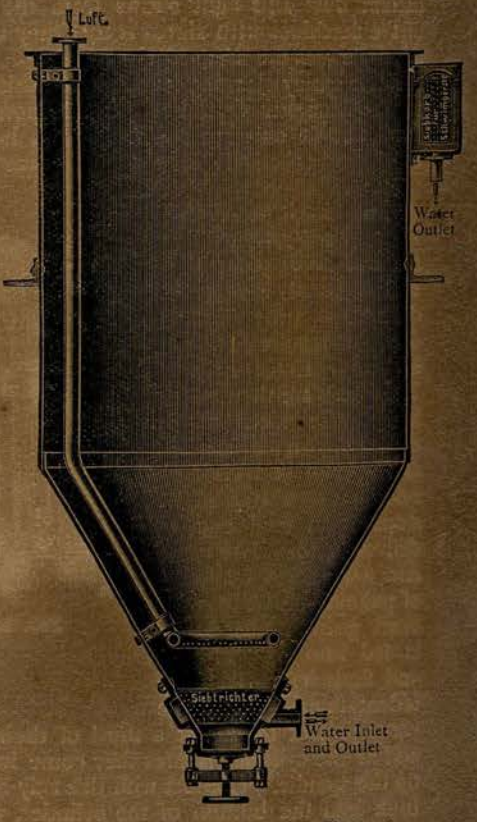

FIG. 102.—German Aerating Cistern for Steeping Barley.
(Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

system of aeration, an idea originating from Germany. It consists of an air compressor and receiver: the air is forced into the steep through a valve fitted to the water inlet pipe and a certain quantity of air goes in with the water. At varying intervals during steeping, air is let into the cistern, causing the barley to move about or "boil up," thoroughly aerating it and assisting the regular germination, besides, as is claimed, shortening the time for steeping and couching.

The size of steeping cistern can be obtained from the fact that a mixture of barley and water in a cistern occupies 14-15 cub. ft. per quarter. The barley after being in the steep about forty-eight to sixty hours, at a temperature of about 50°-54° F., should have the water drained away by means of the valve fitted at the bottom for that purpose, the grain being prevented from going with the water by means of a slotted or perforated gun-metal grid. This grid is attached to a door covering the bottom of steeping cistern, the door itself being carried on a vertical pin secured to the lower part of cone. This pin forms a hinge allowing the door to be swung round horizontally clear of the opening permitting the grains to fall on to the working floor.

Growing or Germinating Floors.—The malt-house usually consists of several floors. The wet grain falling on these from the steeping cistern is levelled down to a depth of 2-3 ft. This is called a **couch**, and the operation is known as **couching**, and is done to cause a sufficiently high temperature to make the grain commence to germinate properly. When the barley begins to sprout or grow, small hair-like rootlets are produced, and heat is generated during growth; the temperature must not be allowed to increase more than a certain amount (60° F.). Hence, when growth has started the couch is broken down and spread over the floor to a depth of about 3-4 in. This is called a piece of malt, and the depth must be varied according to the rate of growth and the varying temperature in the malt-house, as it is obvious that if the thickness is too great and the temperature high, forcing will result; while, on the other hand, if the thickness is not sufficient and the temperature low, then the growth will be retarded, and indeed often stopped altogether.

Moreover, since for uniform growth the malt requires air, it is necessary to aerate the growing barley (which is now known as "**green malt**"). This is

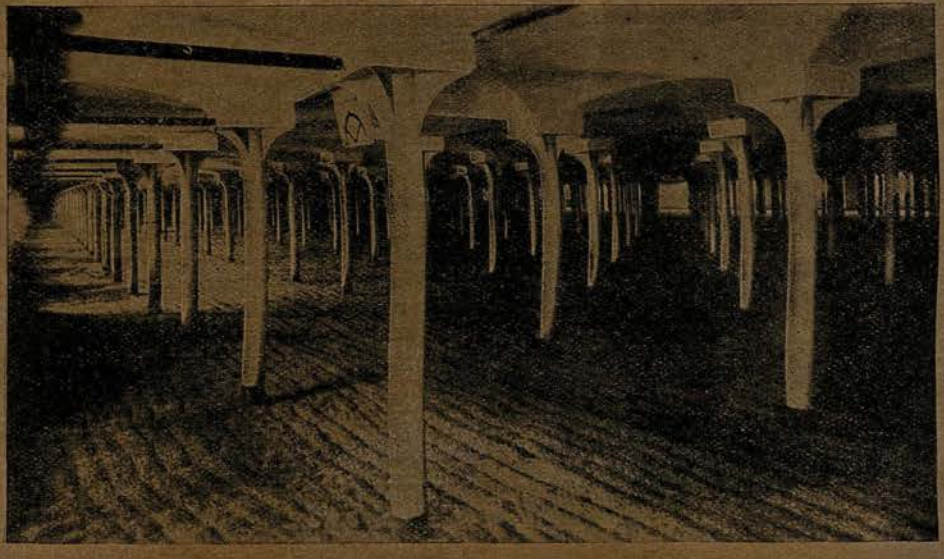

FIG. 103.—Malt House (Malt Growing on Floor), Guinness's Brewery, Dublin.

done by turning the malt with shovels about twice a day. During the turning the green malt is thrown through the air in a thin stream, whereby it is aerated and cooled. It is often ploughed by means of a hand plough which aerates without the need of the heavy labour of completely turning the piece. During the turning process the malt is gradually worked along the floor, being sprinkled when necessary to assist growth, until it arrives at the kiln end of the malting, and it is then considered sufficiently grown. This usually occupies from nine to thirteen days, depending upon the character of the barley, and the quality and character of malt it is required to produce.

The chemical changes which have taken place in the barley up to this stage is the secretion of the enzymes **cytase**, diastase, and peptase. The **cytase** dissolves the cell-walls within the endosperm, enabling the **diastase** to attack the starch, converting it, according to the requirements of the growing plantlet, into diffusible and readily assimilable sugar; at the same time the **peptase** attacks the albumoids (proteids), converting them into soluble **peptones**, **amides** (such as glutamine and asparagine), and amido-acids (*e.g.*, tyrosine and leucine).

The formation of these soluble nitrogenous bodies at this stage are of great importance for the nourishment of the embryo and, later, the growing yeast.

If the growth of the germinated malt continues beyond the limit now attained, a serious loss of starch and sugar will result. The further growth of the barley is therefore checked by—

Withering.—That is, the rootlets are allowed to fade and wither by withholding any further outside supply of moisture to the grain. The withering stage occupies about twenty-four hours, and the malt is then loaded on to the kiln. Moisture at loading-on should be less than 40 per cent. This loading used to be done by hoisting the green malt in sheets or baskets, and indeed is done so at the present time in a good many of the older malt-houses. The modern system is, however, to employ elevators for the purpose.

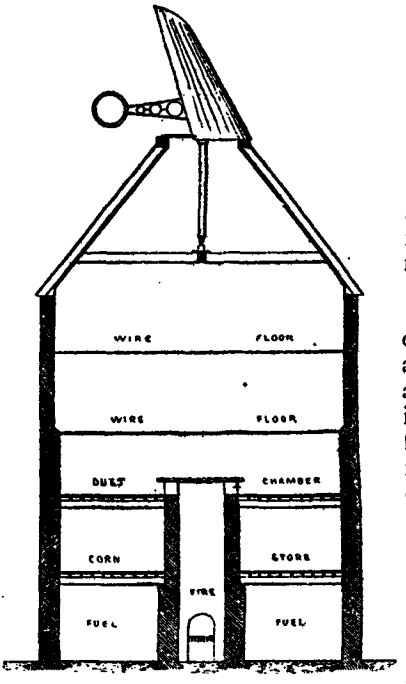

FIG. 104.—Scottish Two-floor Malt Kiln. (Messrs Bryan, Corcoran Ltd., London.)

Kilning or Drying.—The malt remains on the kiln for about three to four days, drying and curing, two days being taken up for drying and two for curing. During the time the malt is on the kiln for this purpose it is turned frequently so as to allow the heat from the furnace to come into contact evenly with the whole of the malt.

The kiln usually has only one floor made of wire or tiles, and heated by means of a closed furnace below. The roof is constructed in the form of a pyramid, having outlet at the top, with adjustable doors for carrying off the vapours. In some modern kilns suction fans are placed in the outlets to accelerate the drying. The green malt is evenly spread upon the kiln floor about 12-18 in. deep and frequently turned during the drying and curing process. In Scotland the kilns usually have two floors made of wire, placed one above the other, and heated by a furnace or open fire from below. The green malt is evenly spread upon the upper kiln floor about 18 in. deep. It remains here twenty-four hours, and is then only partially dried. It is then dropped upon the lower floor, again

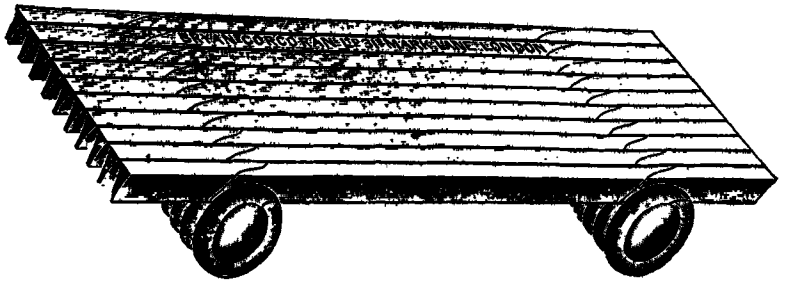

FIG. 105.—Patent Steel Flooring for Malt Kilns.

spread evenly, and subjected to a higher temperature until the desired degree of dryness is obtained.

The heat is obtained by means of shaft furnaces as shown, and good anthracite coal is most generally employed—coke being unsatisfactory owing to the fumes depositing arsenic on the malt.

This latter objection is due to the practice in English malting of allowing the products of combustion to come into direct contact with the drying malt.

For the drying stage the temperature usually commences at about 80° F., rising gradually to 120° F., while for curing, the temperature is raised from the latter figure to 160° or up to 200° F., where high coloured or porter malts are required.

The turning of the malt on the kiln in modern maltings is done by means of an Automatic Kiln Turner, which ensures that the whole of the malt is thoroughly turned, obviating the risk of getting vitrified or unevenly coloured malts which often happens where the turning is done badly by hand.

FIG. 106.—Wire Flooring of Malt Kiln.

The malt being completely dried and cured is allowed to cool, and is then emptied into the bins under the hot air chamber forming the warm malt store.

The emptying is done by means of a number of steel pipes led from the kiln floor to the bins, the malt being shovelled into heaps over each pipe, from which the cover is removed, and while a large amount will run down by gravity the remainder is swept into the pipes by the maltster. From these bins the malt is either lifted up by means of an elevator and distributed by a band conveyor to the main malt stores, or it is first screened and then put into stores. Where the second method is adopted it is often usual to screen again before sending out the malt—although this is not absolutely necessary provided a thoroughly good malt screen is first employed.

The choice of these two methods of dealing with the malt lies with the individual maltster, opinion being very divided as to whether it is better to store the malt with the culms on or not.

The malt stored in suitable bins may be preserved without injury for twelve months or longer.

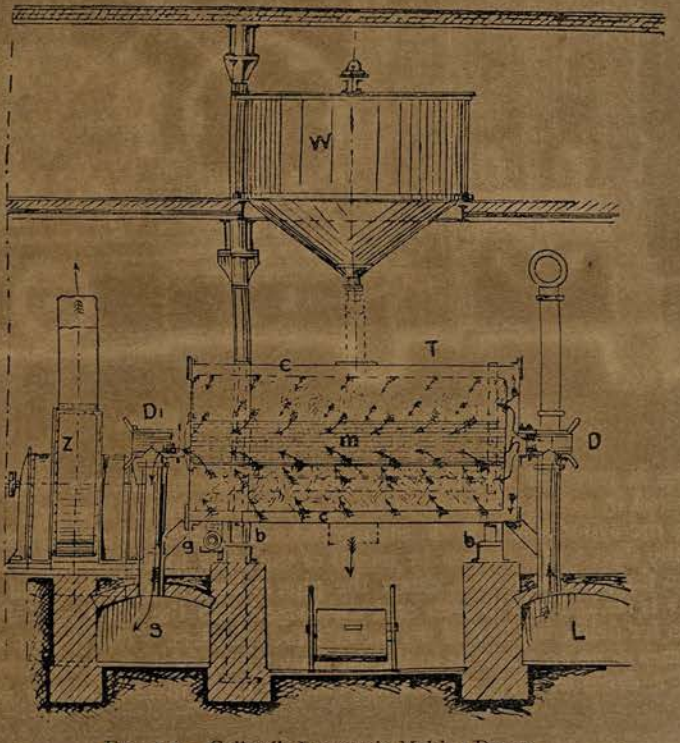

FIG. 107.—Galland's Pneumatic Malting Drums.

Pneumatic Malting

The foregoing is the general system of malting as used in England. There is, however, another system used to some extent in England known as pneumatic malting. In this process the grain, after being steeped in the same way as for floor malting, is put into revolving germinating drums (Figs. 107, 108).

These drums are only partly filled with grain. They are constructed with an outer shell of steel plate and an inner cylinder of perforated metal. Running through the centre of the cylinder throughout its length is a tube of similar perforated metal. Each end of the cylinder is connected by means of pipes to air ducts built below the level of cylinders. One of these ducts, L, is connected at one end to a tower through which the air is compelled to pass, and in passing, this air is purified and moistened, as well as heated by a steam jet when necessary.

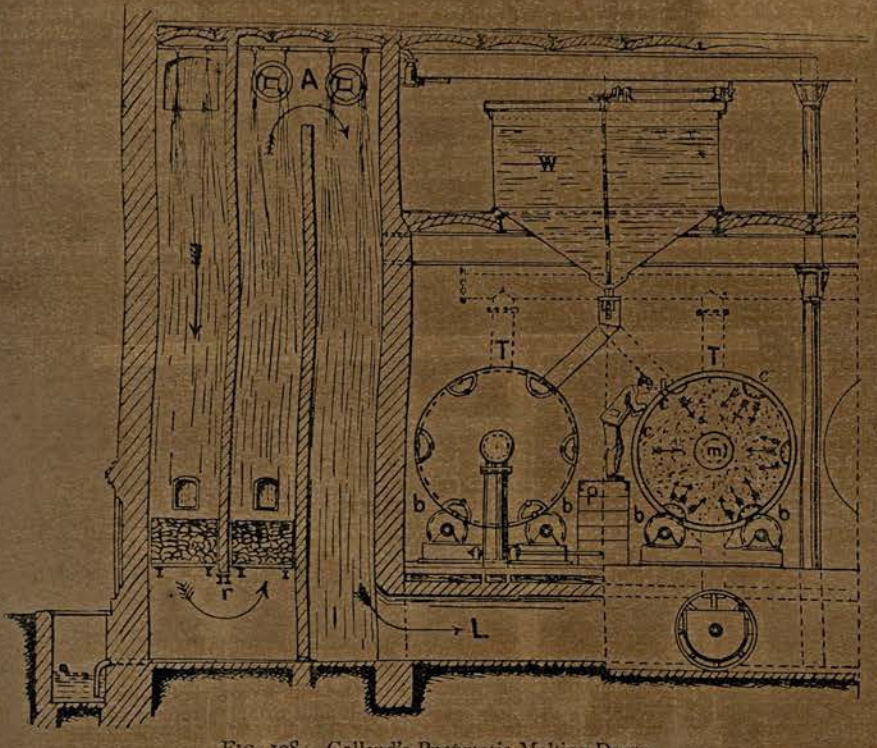

Fig. 108.—Galland's Pneumatic Malting Drums.

The drum is revolved very slowly by means of a worm gear, the weight of drum being carried by rollers mounted on spindles carried in heavy bearings.

When the cylinder is in work, the fan induces a current of air from the air tower through the duct L and thence by means of the pipes to the cylinder, through the grain, into the perforated tube, down the pipe at back of cylinder, and thence by the duct S is sucked into the fan and discharged into the open air. Provision is also made for delivering heated dry air into the cylinders. The drying and curing is sometimes done on a kiln as in the ordinary system of malting and sometimes by means of a drum working substantially in the same manner as the germinating drums.

This system of malting has advantages in economy of space and in saving of labour, but it is regarded as being very expensive in first cost and in subsequent upkeep. There are a number of

plants at work in Great Britain, although maltsters generally do not view the results from them very favourably.

Another system of malting which, like the former, is of German origin, is the Plischke system, a patent device which consists of a number of moving wire beds. The grain is delivered from the steeping tank on to the top bed and this moves over end rollers very slowly. The growing grain is discharged from the top to the next bed and then to the next, and so on till when it is finally discharged from the bottom bed the process of germination is completed and the "green malt" is ready to load on to the kiln.

Another system in vogue in Germany is that in which the malt is grown, *i.e.*, germinated on floors in the same way as in England, but the turning and ploughing of the growing grain is done by a specially constructed and patented machine. In the matter of kilns the German system is generally that the hot gases do not come into direct contact with the malt during the curing process, but they are conducted through pipes running under the kiln floors, which are made of wire, and the air passing over these pipes becomes heated and is drawn through the wire floor and consequently through the malt, thus drying and curing it.

Storing and Conveying Barley and Malt.—In the malt-house described we assume that the barley will be brought in trucks or carts, and stored in bulk, that is in bins, and for this purpose bins with self-emptying conical bottoms are used.

It is usual to allow 10 cub. ft. per quarter for **barley**, and 12 cub. ft. per quarter for **malt**, when storing in bulk in bins.

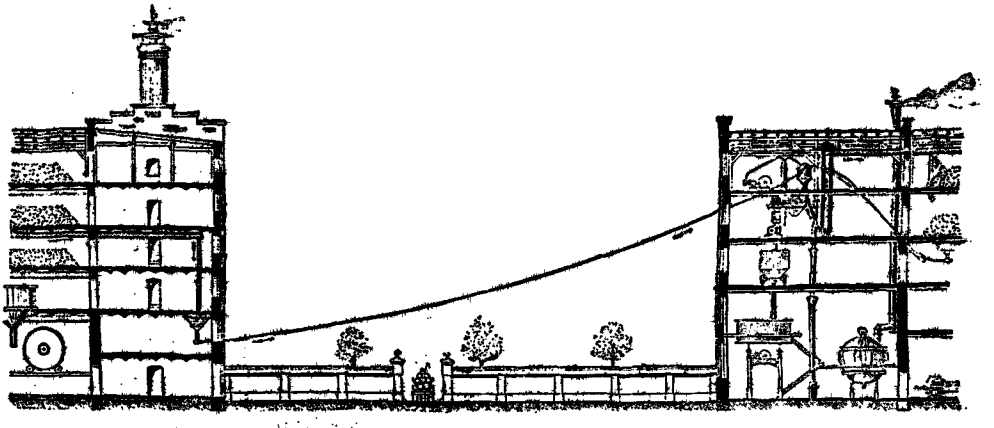

FIG. 109.—Pneumatic Transport of Malt from Malt House to Brewery.
(Seck Engineering Co., London.)

The method of filling the bins has usually been done by means of a sack hoist, but for various reasons this is not advocated, an elevator, or, as it is sometimes called, a Jacob's ladder, being much preferable. This should command a band conveyor in roof with a movable throw-off carriage, delivering into the barley stores by means of pipes, and if this band is made to reverse so as to run in either direction, the roof can be made to serve as a barley store, so as to facilitate buying in large quantities at the commencement of the season. The reason for making the band conveyor reversible is that by means of one or two small intermediate elevators, the barley stored in the roof can be brought back over the cleaning machinery or steeping cistern for steeping.

While elevators and band conveyors are very largely used for conveying and transporting grain, there are a great number of occasions when it is impossible to make use of these appliances.

Where such conditions arise, the system of transporting grain by means of air suction is extremely useful. It can be used for connecting buildings up to 300 or 400 yds. apart from each other, and of varying elevation, without the need of any bridge, such as would be the case with band conveyors, while the absence of large elevator trunks going through floors is a great safeguard against fire. The tubes vary from about 3 in. to 6 or 7 in. diameter, and a great feature in their use is that corners can be readily negotiated, and rigid straight lines need not be adhered to.

The illustration shows very clearly one of the uses that the Pneumatic Transport can be put to.

Composition, Yield, and Analysis of Malt.—In general, 100 parts of air-dried barley yield 70-75 parts of cured malt. In the case of very nitrogenous barleys the loss is greater than this. During the storing, the malt absorbs some per cent. of moisture.

Malt usually contains 75 per cent. of soluble extractive substances, including 10 per cent. cane sugar and invert sugar. The percentage of extract is usually determined in the laboratory by first

grinding it into the finest possible powder, and then extracting with a definite quantity of water at 60°-65° C., and taking the rotation of the filtered solution with the polarimeter. For detailed methods of Malt Analysis see G. Cecil Jones, *Journ. Instit. Brewing*, 1905 and 1907.

100 parts of barley, containing 86 per cent. dry substance, lose :—

In steeping	1.3 per cent.
During germination by the evolution of gases like CO_2	5.1 ,,
Other losses during germination	4.0 ,,
Total loss	10.4 per cent.

One of the best mills for grinding the malt is the "Seck" laboratory mill. These mills are made for either coarse or fine grinding.

The mill, which is made for coarse grist, has been adopted by the Committee on coarse grist analysis. Its value lies in the great care expended in its construction, which enables the maltster to be able to tell, with unvarying regularity, the quality in extracts of the malts he produces.

Another appliance which is intended to work with the mill is the laboratory sieve, which is a sieving machine made with removable beds of various gauges. By putting in different beds, the maltster can grade his barley, his malt, or by the employment of quite fine sieves determine the character of the grist which would be produced from his malt.

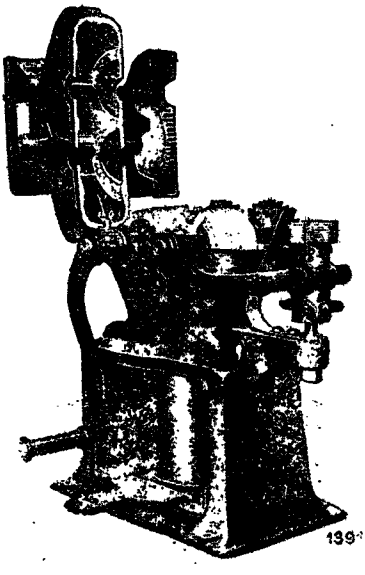

FIG. 110.—"Seck" Laboratory Mill. (Seck Engineering Co., London.)

BREWING

Theory of Brewing.—The malt contains, as we have already seen, a considerable amount of starch and its degradation products. It also contains the enzyme diastase in considerable amounts. The malt is crushed and mixed with hot water (160°-168° F.) in a mashing vat. The diastase now acts powerfully upon the starch, converting it into sugars.

The diastatic degradation of starch is no simple change. According to Brown and Morris the **starch** molecule consists of five amylin groups, each of formula $[C_{12}H_{20}O_{10}]_{20}$, four radicles being grouped centrally round the fifth, thus :—

$$\begin{matrix}[C_{12}H_{20}O_{10}]_{20} \\ [C_{12}H_{20}O_{10}]_{20}\end{matrix}\!\!\diagdown\!\!\diagup\!\![C_{12}H_{20}O_{10}]_{20}\!\!\diagdown\!\!\diagup\!\!\begin{matrix}[C_{12}H_{20}O_{10}]_{20} \\ [C_{12}H_{20}O_{10}]_{20}\end{matrix}$$

Diastase splits up this complex molecule, hydrolysing it into four groups of amyloïns, while the central amylin group remains unchanged (and not being attacked by alcohol-producing enzymes, is left unchanged throughout the whole course of brewing operations), forming what is known as **stable dextrine**, according to the equation :—

Starch. Water. Stable Dextrine. Amyloïns of Various Types.

$$5([C_{12}H_{20}O_{10}]_{20}) + 4\,M.H_2O = (C_{12}H_{20}O_{10})_{20} + 4\begin{cases}(C_{12}H_{22}O_{11})m \leftarrow \text{Maltose radicle.} \\ (C_{12}H_{20}O_{10})n \leftarrow \text{Dextrine radicle.}\end{cases}$$

The amyloïns are compounds of maltose and dextrine, and exhibit the properties both of maltose and of dextrine.

As the process of hydrolysis proceeds the amyloïns pass into lower degradation products which are richer in maltose, the final product of transformation being **maltose**. Several amyloïns have been isolated, *e.g.*, $(C_{12}H_{20}O_{10})_6.(C_{12}H_{22}O_{11})$ (amylo-dextrine) and $(C_{12}H_{20}O_{10})_2.(C_{12}H_{22}O_{11})$ (malto-dextrine).

The amyloïns are not split up in the primary fermentation; in the secondary fermentation they are converted, more or less rapidly according to their type, into maltose. They are of two types, "high" and "low." A beer of a stable character must contain a considerable proportion of high-type amyloïns (which are the first product of the action of diastase on starch), and consequently is produced by restricting the action of diastase in the mash-tub. A beer which is to "condition" rapidly must contain a sufficient amount of low-type malto-dextrine (which are later products of the action of diastase on starch).

The type of malto-dextrine ultimately produced from the starch in the malt can be regulated both in the malt-kiln and in the mash-tub. Higher types are produced by *low kiln* and *high mashing* temperatures, whereas lower types are produced by *high kiln* and *low mashing* heats.

It is therefore possible to regulate on scientific lines both the quantity and the type of amylons which are suitable for a particular beer.

The hydrolysis of the starch by the **diastase** proceeds best between 40°-60° C., but the temperature is often raised to 70° because the starch should be gelatinised, the attack being then more rapid. The starch of the malt dissolves much more easily than that of the raw grain. The dextrines produced, $(C_{12}H_{20}O_{10})_n.H_2O$, are amorphous, reduce Fehling's solution, and are strongly dextro-rotatory. As the molecule breaks up under the action of the diastase the dextro-rotary power diminishes while the power of reducing Fehling's solution increases.

Only the low-grade dextrines are fermentable with yeast.

The following table shows the rotary and copper-reducing power of some of the products of the break up of the starch molecule:—

	Specific Rotation $[\alpha]_D$.	Copper-Reducing Power (Maltose = 100).
Soluble starch, $(C_{12}H_{20}O_{10})_n$	+ 198°	0
Amylo-dextrine, $(C_{12}H_{20}O_{10})_7.H_2O$	+ 187°	9
Malto-dextrine α, $(C_{12}H_{20}O_{10})_3.H_2O$	+ 180°	33
Malto-dextrine γ	+ 170°	60
Maltose, $(C_{12}H_{22}O_{11})$	+ 137°	100

The **Maltose**, $C_{12}H_{22}O_{11}+H_2O$, is easily soluble in water, crystalline, tasting but slightly sweet. It hydrolyses with acids into 2 molecules of dextrose and gives with **phenyl hydrazine** a difficultly soluble dextro-rotary osazone, $C_{24}H_{32}N_4O_9$ (see pp. 166, 167, Glucose).

Under favourable conditions over 80 per cent. of starch can be converted into dextrose by diastase, the other 20 per cent. remaining as dextrine in the liquor. After the destruction of the maltose by the yeast, this dextrine is slowly hydrolysed to maltose.

As will be seen in the next chapter it is the object of the *distiller* to convert *all* his starch into **maltose**, but the brewer, on the other hand, intentionally leads the mashing process in such a manner that a large amount of unfermented dextrine remains in the beer and as "extract" forms the nutritious part of the beer. Hence in brewing matters are arranged so that only about 60 per cent. of the starch is transformed into fermentable carbohydrates.

In order to obtain a dark beer and produce a pronounced malt flavour **caramel** and black malt (*i.e.*, malt browned by heating to a considerable temperature in rotating drums) are added in small amounts mixed with other materials. Malt substitutes, raw grain, and brewing sugars are also added at this stage: (1) for producing very stable beers, since they contain little albumen; (2) for producing paler beers than could be produced with malt alone; (3) for reducing the cost of production. Among such products may be mentioned raw grain, rice, corn grits, corn meal, maize flakes, brewing sugars, etc. Flakes are produced by steaming corn grits and passing them through hot steel rollers; this makes them dissolve better during mashing. Raw grain, corn grits, rice, etc., require previous cooking, whereas flakes are added directly to the wort in the kettle. Brewing sugars are used for producing lager beers, English ale, stout, etc.

The mashing takes about three hours. The hops are added to the boiling wort for the purpose of imparting (1) **tannin**, which forms insoluble compounds with albuminoids, and thus causes them to coagulate out; (2) **hop oil**, which gives the beer its hop aroma; (3) **hop resin**, which imparts to the beer a bitter taste and also acts as a preservative.

While adding the hops the wort is thoroughly boiled, the best hops being added last, so that the volatile hop oil may not be driven off. The boiling sterilises the wort and coagulates the albuminoids, which separate in flakes.

The wort is then run off, cooled to a suitable temperature in a refrigerator (56°-60° F. for English top-fermenting beer), and the yeast is added to the wort in the fermenting tanks. The yeast rapidly develops, and converts the sugars into alcohol and carbon dioxide by what is called "**primary fermentation**," thus converting the wort into beer. The yeast is then separated and this beer stored in tuns, where it ripens, undergoing **secondary fermentation** ("*after*" fermentation).

Waters for Brewing Purposes

Waters adapted for producing pale ales contain calcium sulphate in fairly large quantity. Thus the **Burton waters**, which are extremely well adapted for this purpose, have the following composition :—

	Grains per gallon.		Grains per gallon.
Calcium sulphate	77.9	Sodium chloride	3.9
Magnesium carbonate	21.3	Sodium nitrate	2.0
Sodium sulphate	10.2	Potassium sulphate	1.6
Calcium carbonate	7.62	Silica and alumina	0.98

The best brewing effect is obtained from 40-50 grains of $CaSO_4$ per gallon.

Waters adapted for producing black beers must be soft, containing, however, fairly large amounts of calcium and magnesium carbonates. Since these latter substances are almost entirely precipitated by boiling, the water as actually used in the brewery contains only 2-3 grains of solid matter per gallon. London and Dublin well waters are well suited for beers of this type. An analysis of a Dublin well water gave :—

	Grains per gallon.		Grains per gallon.
Calcium carbonate	14.2	Magnesium carbonate	0.90
Calcium sulphate	4.4	Silica	0.26
Sodium chloride	1.83	Iron oxide and alumina	0.24

Waters adapted for producing mild ales must contain a large amount of chlorides and little calcium sulphate. The following is a typical analysis :—

	Grains per gallon.		Grains per gallon.
Sodium chloride	35.1	Magnesium carbonate	4.0
Calcium chloride	3.9	Iron oxide and alumina	0.24
Calcium carbonate	16.4	Silica	0.22
Calcium sulphate	6.2		

No single water possesses the qualifications necessary for producing every class of beer. To render a water suitable for producing a given type of beer it is necessary to analyse it accurately and then add to it the proper amount of calcium sulphate, magnesium sulphate, calcium chloride, etc., to bring it up to the standard conditions. If a water contains too much calcium sulphate it is usual to *dilute* the water with a soft one so as to reduce the percentage of $CaSO_4$ to the proper amount. In some cases precipitation by Na_2CO_3 is resorted to for removing the $CaSO_4$. The addition of Na_2CO_3, followed by $CaCl_2$, is resorted to for getting rid of excess of iron.

THE PRACTICE OF BREWING AS GENERALLY ADOPTED IN ENGLAND

General Arrangement of the Brewery

In deciding upon a site for a brewery a place must be chosen having a natural supply of good water to draw from, independent of town supply, as the requirements in this respect are very large. The character of beer is governed to a large extent by the quality of the water used in its production. In cases where the water is specially suitable for brewing, large and important brewing centres have been formed. Thus the hard water of Burton-on-Trent has gained for this town a world-wide reputation for pale ales, whilst the softer London and Dublin waters have brought the stouts produced in these centres into equal prominence. As, however, science is now capable of treating water so as to imitate the conditions required, the choice of site is very largely governed by the local demand. The site having been selected and the size and output of brewery having been determined, the general working arrangement of the necessary plant has to be decided upon, and, needless to say, the arrangement should be such as to minimise labour and consumption of power as much as possible.

There are two systems of constructing breweries generally in use, known as the tower and horizontal systems, both having their recommendations. The tower system is worked entirely by gravity, that is to say that the process of manufacture involves treatment floor by floor, descending by stages until the finished beer is ultimately dealt with on the ground floor.

The horizontal system, while it involves a large area, is one enabling the manufacture to be conducted at a low level, very often a great advantage, the process being to erect pumps, elevators, etc., for conducting the material during the stages of treatment from vessel to vessel. Often the system adopted is a combination of the two types of breweries having a minimum of pumping, while at the same time keeping the height of building within reasonable limits.

As a rule the water (or as it is technically known, liquor) is pumped from the source of supply direct into the cold liquor tank at the top of building. From this tank it is drawn by gravity for the purpose of boiling, cooling, and cleaning. The heating of water in the hot liquor tank is performed by steam coils which raise the temperature of the liquor to the desired number of degrees.

The principal ingredients used in brewing consist of malt and hops, although in some cases varying proportions of maize (flaked or in grits), invert sugar, etc., are used, together or separately, these materials in their chemical composition being very similar to malt. For the purpose, however, of this article, we assume that the brewery is one in which malt and hops are used. The malt, the manufacture of which was described in the preceding pages, is brought into the brewery usually in sacks and hoisted to a malt store over the screening and grinding room.

Where the maltings or malt stores are adjacent to the brewery, a great advantage in saving of labour and time and prevention of slackness in malt can be attained by the use of the system of pneumatic transport, introduced into this country by the Seck Engineering Co. Ltd. (see p. 263). In this case the rather dangerous method of hoisting the malt is done away with, and the malt is brought instead from the maltings or stores through tubes by means of air suction, quite free from floating dust.

The malt is then shot from the malt store into a malt hopper which preferably is large enough to contain sufficient for a brew.

The hopper commands the malt screen, which is a machine having revolving wire or perforated cylinders for removing large substances, heavy dirt and culms,

and should be fitted with a polisher to remove any deleterious substances adhering to the skin of the malt (see p. 257).

The clean malt as it leaves the screen is lifted by a short elevator to the malt grinding mill.

This question of grinding has not always received the attention it really merited, and it is only of late years that a really scientific preparation of the grist has been made possible by the adoption of the principle of the Seck Patent Malt Mill. The malt, as it enters this mill, is distributed by means of a very ingenious feed roll, ensuring an accurate and even stream of malt right across the crushing rolls. The mill is constructed with two pairs of rolls, one above the other, and having a sieving device between. The malt is only lightly crushed by the first pair of rolls, and the resulting ground material, which is called grist, falls on to the sieve. This sieve has a reciprocating motion and has the effect of separating the granular grits of the malt kernel, which are sufficiently reduced for brewing purposes, from the husks. These grits pass through the sieve and receive no further treatment, while the husks with any hard steely ends or large coarse grits adhering, pass over the sieve and so to the lower pair of rolls where they are recrushed, the rolls being set closer together

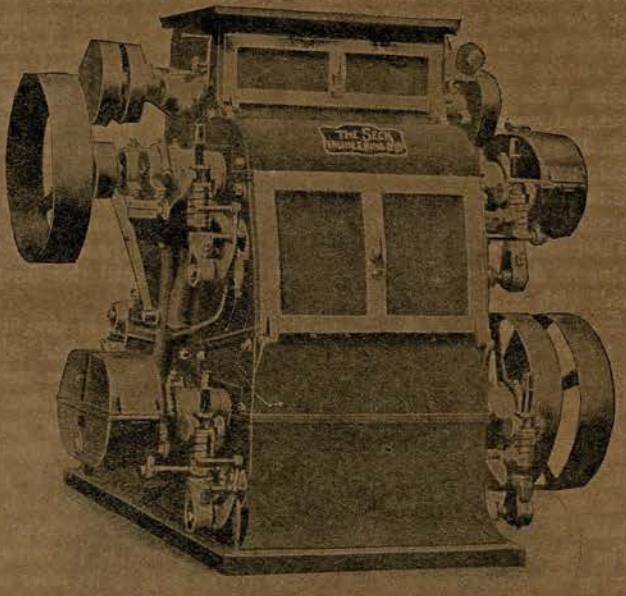

FIG. 111.—Seck Patent Malt Mill. (Seck Engineering Co., London.)

for this purpose. This system of grinding ensures the maximum extract being obtained from the malt, and at the same time gives large flaky husks so essential to a proper filtration or drainage in the mash-tun (see Figs. 111-113).

Mashing.—The grinding is usually performed a few hours before mashing, and the grist case should be protected from the effects of damp, as the grist readily absorbs any moisture, and this has a very detrimental effect on the resulting extract, and also on the quality of the finished product. At the bottom of the grist case is fitted a *Steel's* mashing machine (Figs. 114, 115).

This consists of a cylinder having a spindle running through from end to end, and on this spindle are mounted forks and blades placed at an angle for propelling and mixing the grist as it passes through the said cylinder on its way to the mash-tun. This spindle is provided with driving pulleys. In mashing, the hot liquor, at a temperature of 160° F., is introduced into the sides of mashing machine in the form of a spray, at the same time the grist is allowed to fall from the grist case. The mash, as it is now called, is propelled, as before described, through the machine into the mash-tun.

The mash-tun itself is a circular vessel made of cast iron or copper, and provided on the outside with lagging and insulating material for the purpose of retaining the heat of the mash, while the top has a cover made with doors to lift up to give access to the tun (see Figs. 115, 116).

The interior of the tun is fitted usually with a machine known as a rake. This consists of a vertical shaft rising through the centre of tun, carried on a footstep bearing, and provided with driving gear.

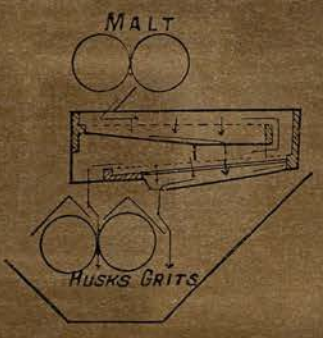

FIG. 112.—Diagram showing Method of Working in Seck Mill for usual Brewery purposes.

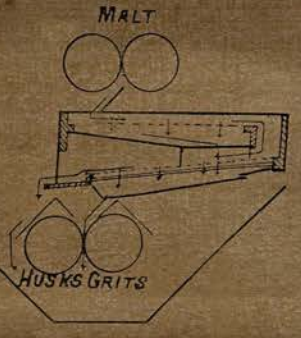

FIG. 113.—Diagram showing Slide in position for R grinding Grits.

The end of the vertical shaft inside tun is connected by bevel gear wheels to a horizontal shaft which revolves on its axis, and at the same time travels round the interior of the tun. This shaft is fitted with a number of forks which are intended to stir up the mash and distribute it evenly over the interior of the tun. At about 1¼ in. from the bottom of tun is fitted a slotted plate covering the whole surface area of the bottom, the slots being small enough to prevent any of the solid portion of the mash from going through, but large enough to allow the wort to percolate through, wort being the name given to the liquor at this stage.

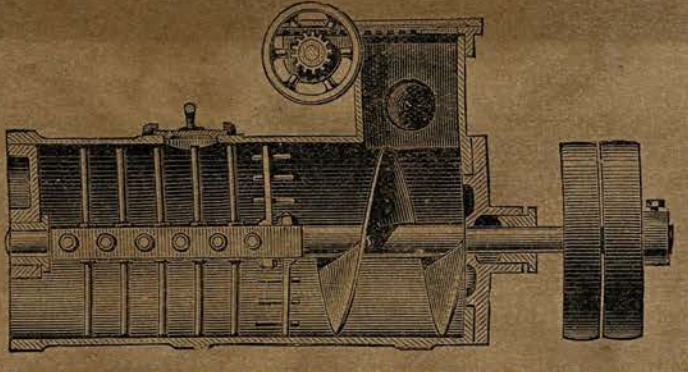

FIG. 114.—Llewellins & James' Improved "Steel's" Mashing Machine. (Llewellins & James, Bristol.)

In the early stage of mashing, **underletting** is sometimes resorted to, and this consists in introducing hot liquor into the bottom of the tun by means of pipes fixed at regular intervals in the actual bottom plates, and generally at some degrees higher temperature than is used for mashing. These pipes are also used for heating the tun before mashing. The mash is now allowed to stand for about two hours. The next process consists of washing out the wort from the mash (or "goods"). For this purpose an apparatus known as the **sparger**, which is fixed

inside the mash-tun at about the level of the top, is used, and consists of two perforated copper pipes, fitted to a revolving centre, and through which liquor is introduced. The perforations are at one side and bottom only of the pipe, the

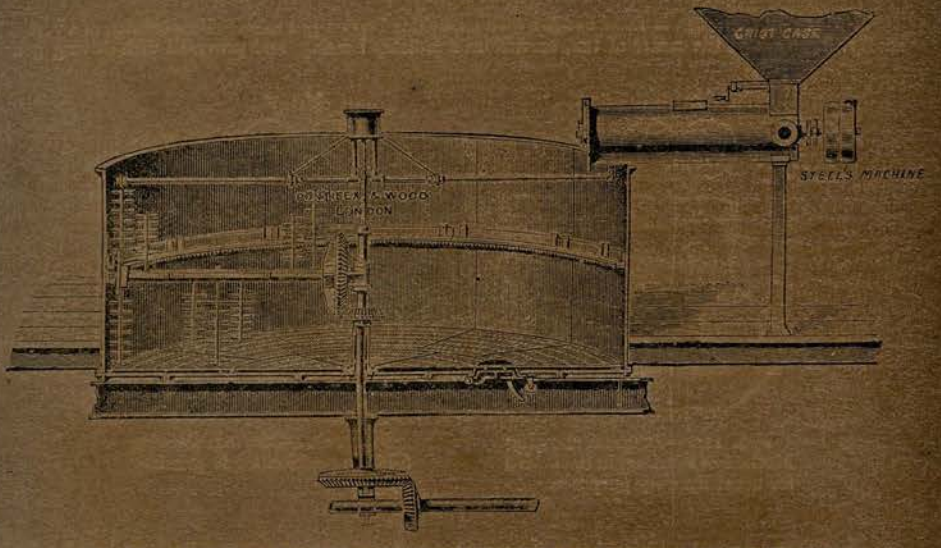

FIG. 115.—Cast-Iron Mash-Tun, showing Internal Rake Mashing Machine, Steel's Machine, Copper Sparger, Copper Slotted False Bottom, etc.
(Haslam Foundry and Engineering Co., Derby.)

hot liquor flowing out acting as a driving power causing the pipes to revolve and distribute the hot liquor in a very fine spray over the goods. The sparging liquor has generally a temperature of 170°-195° F.

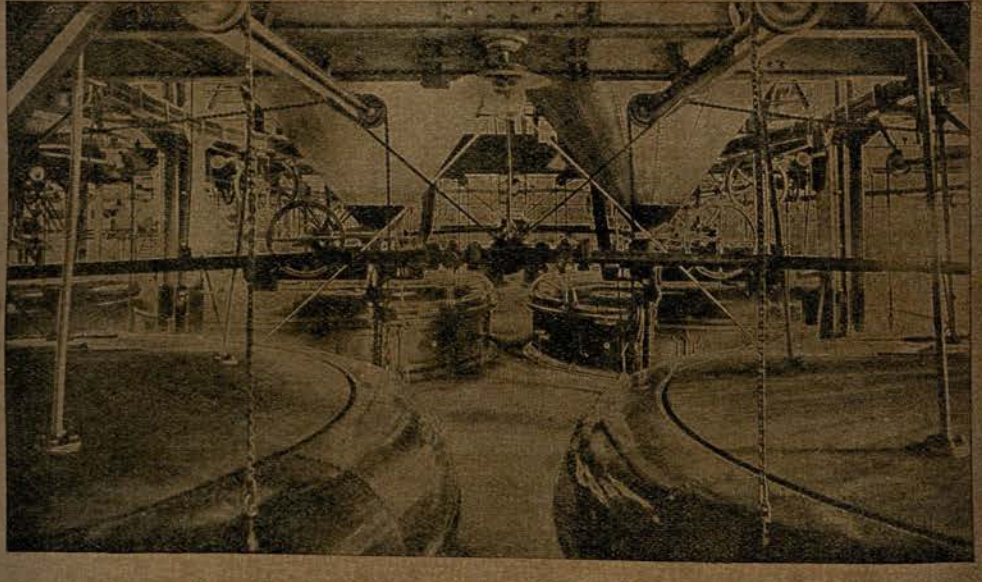

FIG. 116.—Mash-Tuns for Malt, at Guinness's Brewery, Dublin.

The wort is carried away by means of the pipes in the bottom of tun through a sampling pan, and by gravity direct to the underback and from thence to the copper. The **underback** is a vessel made either in cast iron or copper, and is provided as a source of supply to the copper, and as a means of safety, preventing the danger of burning the bottom of copper when finished wort is discharged. It is also used in some breweries for the purpose of continuing the action of the diastase after the wort leaves the mash-tun, and in this case is provided with either a steam coil or steam jacket for the purpose of maintaining the correct temperature.

In some breweries where raw grain is used, an apparatus called a "**Raw Grain Converter**" is often used (Fig. 117). It consists of a strong vessel heated internally by steam, as shown.

The malt and grits are mashed together in the apparatus, and when conversion is effected, let down into the ordinary mash-tun underneath, which simply acts as a filter; the wort is then pumped back into the converter and boiled, as in the ordinary copper, the hops being added in the usual way. The contents are again, after boiling, let down into the mash-tun, which in this instance acts as the hop back. The apparatus thus acts first as a raw grain converter, secondly as a mash-tun, thirdly as an ordinary boiling copper. No hop back is needed, as the mash-tun serves for this purpose.

The use of raw grain in the manufacture of malt liquor, provided it is wisely done, is stated to be decidedly advantageous to the quality of the beer produced, and is also very economical. With this apparatus as much as 50 per cent. of raw grain can be used, and it can also be used in lieu of the copper for boiling the wort.

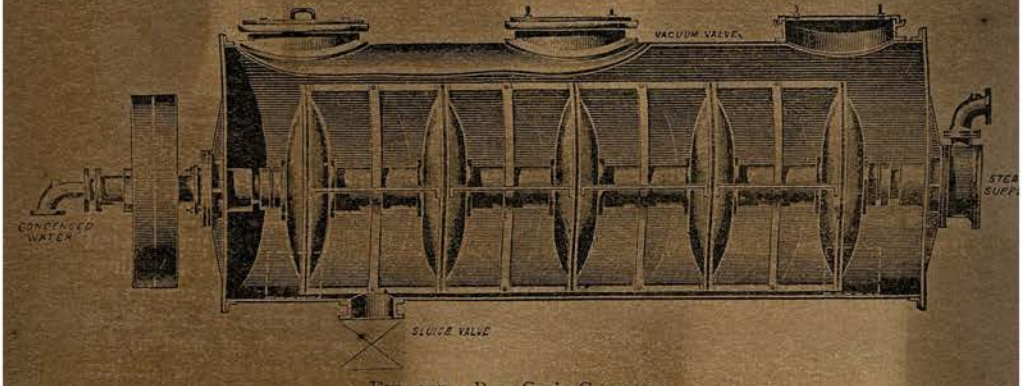

FIG. 117.—Raw Grain Converter.
(Haslam Foundry and Engineering Co., Derby.)

Boiling and Hopping the Wort.—The **copper** is a vessel made in either cast iron or copper, principally the latter, and is heated either by a furnace underneath or by steam coils or steam jacket (Figs. 118, 119).

The wort having been run from the underback into the copper, is brought to the boil and the hops introduced at various intervals during the boiling period, the best hops being added last, so that the volatile hop oil is not all driven off. The amount of hops added to English ale and porters amounts to 10-15 lbs. per 1,000 gals., or, say, 10 lbs. hops for each quarter of malt. *German* brewers use far less than this, namely, 1½-8 lbs. per 1,000 gals. The whole is allowed to boil generally for two hours and is then discharged into the hop back. This is a vessel large enough to contain the complete contents of the copper. It is made from cast iron or copper, and is fitted with a perforated false bottom fixed at 1½-2 in. above the true bottom of the vessel. In this vessel the wort is allowed to stand for ten to fifteen minutes to allow the hops to settle on the false bottom, where they then form a filtering medium through which the wort runs off bright, the spent hops retaining most of the sedimentary matter.

Cooling the Wort.—The wort is now pumped for the first time by means of a three-throw pump up to the cooler, into which it is sprayed out through a perforated pipe or a spreader. This has for its object a partial aeration of the wort

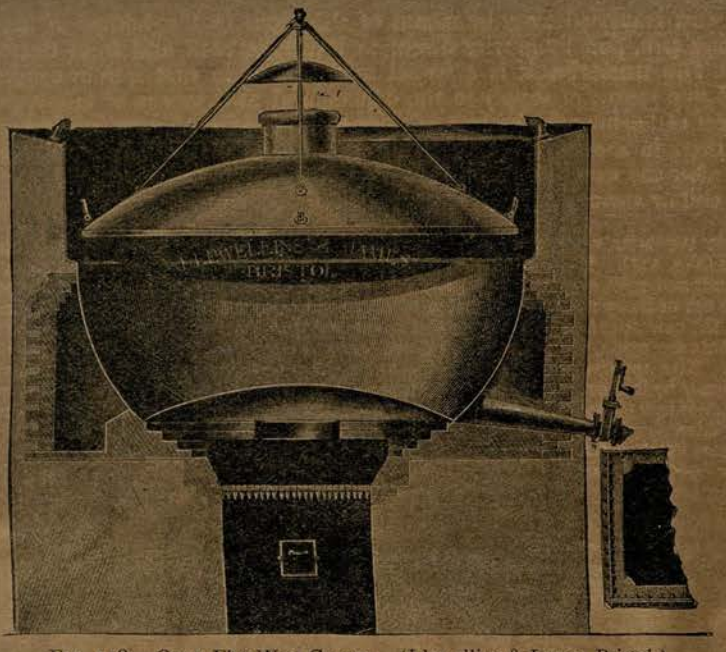

FIG. 118.—Open Fire Wort Copper. (Llewellins & James, Bristol.)

before it settles into the cooler. The cooler is a vessel made of either cast iron, wood, or copper, and large enough to contain the whole of the contents discharged from the copper. The use of the cooler is partly to collect solid matter precipitated by the aeration and drop in temperature, and to act as a source for regulating the supply of wort to the refrigerators or coolers situated immediately below. The refrigerator can be made either horizontal or vertical. The *vertical* type, as shown in Fig. 120, consists of a battery of copper tubes, one above the other, of such a shape to present a maximum of cooling surface to the falling wort. The inside of tubes receives a constant supply of cold liquor derived from the cold liquor tank, while the wort is distributed by means of a specially perforated pan at the top, which is regulated to allow a thin stream to trickle over the exterior of the tubes. By means of this arrangement it is possible to aerate and

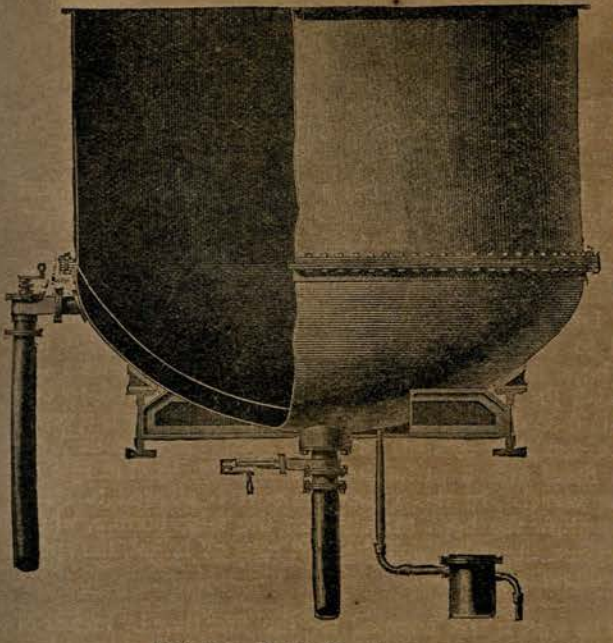

FIG. 119.—Steam Wort Copper.
(Haslam Foundry and Engineering Co., Derby.)

cool the wort from the temperature in the cooler to the temperature at which it is desired to pitch or collect into the fermenting vessels. This is usually 56°-60° F.

Composition and Analysis of the Wort.—The strength of the wort is determined by taking its specific gravity at 17.5° C. This gives its concentration in sugar and the amount of malt extract.

Worts for light beers contain about 10 per cent. extract, heavier beers (*e.g.*, German *Bayerisch*) 12-14 per cent., while some English beers have worts containing 16-18 per cent. and more extract.

The duty on beer is levied at the rate (1910) of 7s. 9d. for each barrel (36 gals.) of wort at a sp. gr. of 1.055 (or, as in the trade, at a gravity of 1,055), an allowance of 6 per cent. being made for waste and loss during fermentation. The volume of the wort is measured by the excise officer in the fermenting vats or collectors before fermenting, the number of gallons of wort corresponding to each inch of depth of the vat being carefully gauged, and the number of gallons of wort actually contained in the vat is found by the dipping rod, a boxwood rule divided into inches.

If the wort has a greater gravity than 1,055 (*i.e.*, sp. gr. 1.055) it must be reduced to its equivalent in gallons at the standard gravity of 1,055. The calculation is made by multiplying the volume of brew in gallons by the excess of gravity over 1,000 (sp. gr. 1.000 = pure water) and dividing by 55. Thus suppose a brew of 4,000 gals. has a gravity of 1.060 (sp. gr. 1.060). Then $4000 \times (1060 - 1000) = 240{,}000$. This figure is divided by 55, the excess of standard gravity over 1,000. This gives $\frac{240{,}000}{55} = 4327.2$. That is, 4,000 gals. of wort of sp. gr. 1.060 are equivalent to 4327.2 gals. of wort at the standard gravity of 1,055, and it is on this figure that the duty is levied, less 6 per cent. for waste deducted. A quarter of malt (336 lbs.) is supposed to yield four barrels of wort of sp. gr. 1.055.

FIG. 120.—Refrigerator or Cooler.
(Haslam Foundry and Engineering Co., Derby.)

The excise authorities reckon as equivalent to a quarter of barley (336 lbs.): 224 lbs. cane sugar; 256 lbs. glucose (invert sugar); 256 lbs. flaked maize or rice; 272 lbs. syrup No. 1, weighing 14 lbs. per gallon; 328 lbs. of syrup No. 2, weighing 13 lbs. 2 oz. per gallon.

The following is the composition of a typical wort:—

Specific gravity	1.056
Maltose	8.880
Non-maltose	4.82
Nitrogenous matter	0.830
Ash	0.234 with 0.085 P_2O_5.

Ratio of maltose : non-maltose = 1 : 0.54.

Everything that reduces Fehling's solution (alkaline copper sulphate solution) is counted as "maltose" on the basis of the reducing power of pure maltose. As a matter of fact, however, a considerable amount of the reduction arises from unfermentable dextrines, cane sugar, glucose, and pentoses, and no simpler method is known of differentiating between the individual effects contributed by the different sugars and the dextrines. The fermentability is best determined by actually fermenting the wort with yeast, and estimating the alcohol. Here, however, the difficulty is that different yeast races produce very different amounts of fermentation. The nitrogenous substances are principally peptones and amides, and are very important foods for the yeast. The ratio of maltose : non-maltose varies from 1 : 1 to 1 : 0.3.

Fermenting the Wort.—The cooled wort is now drawn from the pan in which the refrigerator stands into the top fermenting or collecting vessels. As soon

as the wort has started running into the collecting vessel, the yeast (which has first been thoroughly well roused and mixed in with some of the wort in a small separate vessel) is added. This is for the purpose of setting up the action of fermentation. When all the wort has been collected, it is allowed to stand until a yeasty head begins to form, the time required for this being in various cases from twenty-four to forty-eight hours. Immediately this head begins to form, the wort is run into the dropping fermenting vessel immediately below, leaving any extraneous matter in the top vessels, thus giving a cleaner wort for the final fermentation. For the purpose of removing the yeast thrown up by the fermentation an apparatus called a skimmer and parachute is provided. The skimmer is a wooden blade which passes over the top of the wort and just pushes the yeast head into a parachute, which is a funnel-shaped vessel having a tube running through the bottom of the fermenting vessel into the yeast vessel below.

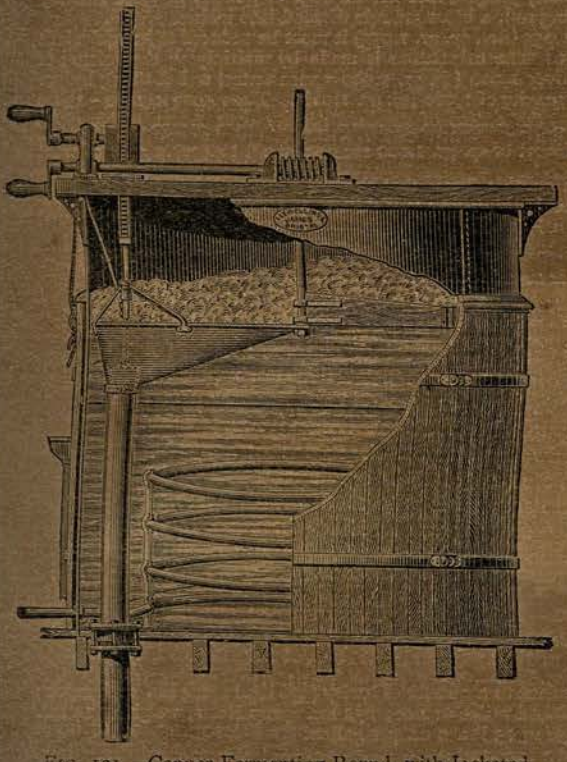

FIG. 121.—Copper Fermenting Round, with Jacketed Wood-Casing, Skimmer, and Parachute. (Llewellins & James, Bristol.

The fermenting vessels are also fitted with coils of pipe called attemperators through which cold and hot liquor may be run to raise or lower the temperature of the fermenting wort to the desired degree. This varies from 56°-75° according to the strength of the beer. The wort, which has now by the process of fermentation been converted into what we know as beer, is now ready for putting into casks. This part of the process is usually described as racking. For **Rate of Fermentation** see p. 240.

In England, where top fermentation is employed at a high temperature, the process usually lasts about eight days. In Germany, however, where "bottom fermentation" is almost exclusively employed, and the temperature is kept as low as 5°-6° C. (41°-43° F.), the fermentation takes about twelve days.

The progress of the fermentation is followed day by day by the alteration in the specific gravity of the clear filtered wort, using the saccharometer for the purpose. On the Continent, **Balling's** saccharometer is employed, and it reads directly the "apparent extract" as degrees "Balling," *e.g.*, in the wort sample, p. 275, the "apparent extract" on the first day is 13.7, and on the twelfth only 6. The amount of "true extract" is also determined with the saccharometer, after removing the alcohol by boiling (the alcohol having a specific gravity less than 1), and making up the volume to its original amount with distilled water. In the wort sample on p. 275 itamounts to 7 on the twelfth day; and, consequently, 13.7 − 7.0 = 6.7 per cent. of extract has disappeared, having been converted into alcohol. Hence the "degree of fermentation" of the wort is:—

$$\frac{\text{loss of extract}}{\text{original extract}} \times 100 = \frac{6.7}{13.7} \times 100 = 49.0.$$

The storage period in cask varies to a large extent, some beers being sent out immediately after racking, and others being kept in cask for a long time, sometimes twelve or eighteen months or longer. Racking is mostly done in the cellars, which should be kept at an even temperature all the year round.

ALTERATION IN A WORT DURING FERMENTATION

	Original Wort.	Eighth Day.	Twelfth Day.
Specific gravity	1.056	1.028	1.025
Per cent. Balling (apparent extract)	13.7	6.7	6.0
True extract	13.7	7.6	7.0
Alcohol	0	2.95	3.25
Maltose	8.88	3.34	2.19
Nitrogenous substances	0.83	0.66	0.60
Ash	0.234	0.222	0.220
P_2O_5	0.084	0.079	0.078
Maltose : non-maltose	1 : 0.54	1 : 1.27	1 : 2.10
Degree of fermentation	...	44.5	49.0

The beer, or barm ale as it is called, is drained or pressed from the yeasts which have been skimmed off through the parachute into the yeast back, and is returned to the fermenting vessel, whilst the yeast, or such as is wanted, is carefully placed in a cool place for use in a future brew. The residues from the brewing operations are spent or exhausted grains, hops or yeast or, as it is commonly called, barm, and there are various markets open for these commodities.

In Germany a portion of the excess yeast is used for making yeast extracts (*Ovos*, *Siris*). More recently, prepared yeast has been placed on the market as human food, as a substitute for meat. For this purpose the yeast is freed from the bitter hop taste by treating with sodium carbonate solution. About 10,000 tons of yeast from German breweries can be utilised annually in this way.

Bottled Beer for export is usually pasteurised by heating on the water bath for a half to one hour at 50°-60° C. The use of antiseptics such as salicylic acid, boracic acid, saccharine, etc., for preserving beer is unnecessary, and, indeed, highly injurious.

A good percentage of alcohol, strong hopping, and perfect cleanliness in manufacture render the beer quite stable.

One great essential for successful brewing is cleanliness.

FOREIGN SYSTEMS OF BREWING

Manufacture of German Lager Beer

The general trend of brewing within recent times has been in favour of light, bright beers, containing less alcohol and hops than the older types of beer.

This trend has resulted in the almost universal production in Germany of beer, which is not only more palatable, but also less intoxicating and more easily digestible than most kinds of English beer.

German beer (termed "Lager" in English, but "Export Bier" in Germany, the term "Lager" being reserved in that country for a somewhat different sort of beer) is produced on entirely different principles from English beer. English beer is produced by a process of "Infusion," whereas German beer is the result of the "Decoction" system.

The process is as follows:—

Mashing.—The "grist," or ground malt, is mashed with cold water until thoroughly mixed, the temperature of the mash-tun being kept at 85°-100° F. by the addition of hot water.

One-third of the mash is then run into the mash copper (*Maisch Kessel*), and heated at 166° F. until the milky fluid becomes transparent, the starch being then rendered soluble by the diastase.

The **Dickmaische** (as the fluid is now called) is boiled for a quarter to three-quarters of an hour, then a portion run back into the mash-tun proper, so as to raise the temperature of the whole to 110°-125° F. After a few minutes another third is withdrawn and treated as before, forming the second **Dickmaische**. This is again returned to the mash-tun, and the whole thoroughly worked up, and allowed to stand, so that coagulated albuminoids, etc., may settle out. Then another third, which from its being a practically clear mash is called the **Lautermaische**, is withdrawn and thoroughly boiled to precipitate all albuminoids, and then again returned to the mash-tun, where the mashing is continued until the final temperature is just over 160° F. The hops are added, and the wort run off and cooled to a low temperature, and yeast added.

Fermentation of the Wort.—Here again the procedure differs entirely from the English practice. In the English *top-fermentation* system the wort is pitched and fermented at a relatively high temperature, viz., 55°-66° F. Moreover, pure yeast cultures cannot be used with success because the fermenting vessels are of great size, and present a large surface to the air for infection. Also the yeast comes to the top of the liquor and there develops (top-fermentation), forming the head. The primary fermentation is very vigorous and rapid, being complete in two to three days, while the secondary fermentation is (in the case of running ales at least) over in fourteen days. Consequently the high temperature and surface exposure of the yeast (which are essential features of the English system) cause infection by foreign yeasts, and a rapid deterioration of any pure yeast culture used results. Also it is generally believed that there is no single type of yeast which will produce characteristic English beer. The simultaneous action of several species of yeast are necessary. Hence it is clear that in English breweries pure single yeast cultures have not been a success (although the use of *mixed* pure cultures has been more promising).

On the **Continental system**, however, all is quite otherwise. Here the yeast is a *bottom-fermentation* sort, and the pitching and fermentation takes place at very low temperatures in cellars cooled artificially to 37°-38° F., and the fermentation vats are small in area. The yeast formed in the fermenting wort (the temperature

of which is seldom above 50° F.) lies at the bottom of the fermenting tun (hence the name bottom-fermentation yeast).

All these conditions are eminently suitable for the employment of pure yeast cultures and the maintenance of it in an uncontaminated state. Hence the practice of brewing with pure yeast is universal in Denmark, Norway, Sweden, and is used in most of the breweries in Germany and Holland and in many cases in America.

After eleven to twelve days the primary fermentation of the yeast is complete, and the beer is stored in casks in an ice-cold cellar for one and a half to six months or more, according to the class of beer produced.

Nathan (German Patent, 135,539, November 1902) produces a good tasting beer in so short an interval as eight days by rendering the wort completely sterile in completely closed enamelled vessels, adding the yeast and blowing sterile air through the apparatus, whereby the yeast very rapidly develops. The process has excited much attention. For details see patent.

Differences between English and Foreign Beers.—It should be observed that the English beers, produced on the **infusion** system, contain more alcohol and are more stable than the German or **decoction** beers. The latter also contain more unfermented malt extract and so are more nutritive than English beers; they are also less heavily hopped and more heavily peptonised than English beers. Since they are produced at very low temperatures they hold in solution a larger amount of carbon dioxide than English beers.

English beers, however, are more stimulating and far more durable. For example "lager" beer cannot be kept on draught, and will not keep unless placed on ice. Consequently if a cask of **lager** beer is opened it must be rapidly consumed, for in a very few hours it becomes undrinkable, the gas rapidly escaping and the beer becoming flat and unpleasant. In Germany, therefore, every publican must have a supply of ice, which is frequently delivered by the brewery together with the beer.

Certain "alcohol-free" beers which are manufactured are either merely malt extract or very weakly fermented beers containing but very little alcohol.

Composition of English and Foreign Beers.—The following analyses will give a general idea of the different compositions of the various English and Continental beers:—

	Beer.	Total Solids (Extract) per Cent.	Alcohol per Cent.
English Beers.	Pale ale	4.32	5.58
	Light bitter	3.96	3.34
	Stout	5.27	6.11
German Beers.	Munich lager	6.95	3.40
	,, export	7.48	4.12
	Pilsener	5.10	3.49
	Berlin Königstadt (light)	4.19	5.28
	,, ,, (dark)	7.73	3.94
	Nürnberger (dark)	6.09	3.51
	Berlin weiss beer	4.21	2.82

V.—SPIRITS AND INDUSTRIAL ALCOHOL, INCLUDING DISTILLING PLANT

By G. Martin, Ph.D., M.Sc., and W. H. Stephens, A.R.C.S.

LITERATURE

(See also under **Distillation**, p. 295)

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Uses of Alcohol.—The greater part of the spirits now produced is consumed as a beverage in the form of brandy, rum, whisky, cognac, cherry brandy, etc. etc. Part, however, is used in making "liqueurs," which are alcoholised wines.

Alcohol is also used on a very large scale technically for heating purposes ("methylated spirits") in spirit lamps, for alcohol lamps, for motor engines, for the manufacture of ether, chloroform, chloral hydrate, glacial acetic acid, aniline colours, celluloid, xylonite, collodion, fulminating powder and explosives, transparent soap, synthetic camphor, artificial silk, synthetic aconite, belladonna, and other drugs, photographic emulsions, lanoline, vinegar, artificial lubricants, furniture polish, varnish, lacquers, enamels, quick-drying paints, dissolving resins for hat makers, goldbeaters' skin, extracting vegetable alkaloids, etc. etc. It will be seen, therefore, that apart from its use as a beverage, alcohol is one of the most important chemicals, and its cheap production is absolutely essential for the development of many new industries. For such industrial purposes it is left tax free, but is made undrinkable by the addition of unpalatable substances (see **Denatured Alcohol**, p. 281). For such technical purposes Germany in 1904-05 used no less than 32,000,000 gals. of industrial alcohol, and the United Kingdom in 1908-09, 6,280,000 gals., while 440,000 *gals. of alcohol* (21,000 gals. being methyl alcohol) were used in a pure state in the manufactures, or for scientific purposes (hospitals, etc.).

The use of alcohol as a motor fuel, *i.e.*, as the explosive agent in an internal combustion motor, is a modern development of engineering practice. It is cleaner than petroleum, and far less dangerous to use than gasolene, but alcohol motors are difficult to start, and as a power producer it is slightly inferior to gasolene, and slightly dearer. Should, however, as seems probable, the price of gasolene rise, there is little doubt that alcohol motors will come widely into use, and great improvements in design are, no doubt, possible, since an explosive mixture of alcohol vapour and air can be used under far higher compression without auto-ignition than a similar mixture of gasolene and air. The heating value of alcohol lies between 13,310 and 10,080 B.T.U. per pound. The following table is instructive :—

MOTOR FUELS.

Fuel.	Heating Value per Pound, B.T.U.	Cost per Gallon.	Specific Gravity.	Cost of 10,000 B.T.U.
Gasolene	19,000	7½d.	0.710	0.668d.
Kerosene	18,500	6½d.	0.800	0.501d.
Alcohol (90 per cent.)	10,080	7½d.	0.815	1.095d.

Alcohol lamps have a fairly extended use on the Continent, the colourless hot flame of the burning alcohol being used in the same way as our ordinary bunsen gas burners to heat an incandescent mantle. A very powerful light is thus obtained. Such lamps, however, have to be started by burning a little alcohol in a pan, thus heating the alcohol until part gasifies. They are not, therefore, so convenient as oil or gas lamps.

Undoubtedly the most extended use of industrial alcohol is for heating purposes, such as boiling water in small spirit lamps in the household.

The amount of alcohol (pure) consumed per head of the population of the chief countries of the world is shown by the following statistics :—

ALCOHOL CONSUMED PER HEAD OF POPULATION.

	In Brandy, Spirits, etc.	In Beer, etc.	In Wine.	Total.
	Litres	Litres	Litres	
England	2.4	6.3	0.3	9.0
Germany	4.0	4.8	0.6	9.4
France	3.8	1.0	10.3	15.1
Austria-Hungary	3.8	1.8	2.2	7.8
United States	2.6	3.3	0.3	6.2
Denmark	7.2	3.9	...	11.1
Sweden	4.0	1.5	...	5.5
Russia	2.4	0.2	...	2.6

The production of industrial alcohol, containing 80-97 per cent. of alcohol, first became a great industry when the stills were improved so that it became possible to obtain alcohol of this strength at a single operation directly from the alcohol-weak fermented mash. At the present time, especially on the Continent, the centre of gravity of the spirit industry lies in distilleries producing "silent spirit" of over 80-90 per cent. alcohol, and not in those directly producing whiskies brandies, etc., containing 20-60 per cent. of alcohol. The latter are now produced as a rule from "silent spirit" by suitable dilutions with water, etc.

The ordinary brandy, whisky, etc., contain from 20-60 per cent. of alcohol In so concentrated a form the alcohol acts as a poison to the nervous system in a manner similar to opium or tobacco, producing at first a stimulating effect, which afterwards generates a craving for the drug, and causes the distressing effects of alcoholism which are matters of common knowledge.

Alcohol of more than 60 per cent. also produces poisoning by its dehydrating

effect. Small amounts of alcohol, such as exist in beer and wine, if taken in moderation, cannot be regarded as injurious to health.

The following statistics relating to alcohol are of interest as showing the progress of the industry in the chief civilised countries:—

England produced in 1906-07, 1,413,000 hl.,* 100 per cent. alcohol (1 hl. = 220 gals.), principally grain alcohol.

The **United States** (1908-09), 2,647,000 hl., also principally from **grain**.

Austria-Hungary (1908-09), 2,647,000 hl. (from maize and sugar beet molasses).

Russia (1906), 4,182,000 hl. (half from potatoes, half from grain).

France (1908-09), 2,538,000 hl., principally from sugar beet, as shown in the following table:—

1,259,000 hl.	(100 per cent.)	from	sugar beet.
448,000	,,	,,	,,	molasses.
363,000	,,	,,	,,	potatoes and other starchy material.
212,000	,,	,,	,,	wine.
256,000	,,	,,	,,	apples, pears, wine lees, etc.

It will be seen that by far the greatest amount of spirits is in this case produced from the sugar beet, both from its sugar-rich juice and from molasses, the uncrystallisable residues of beet sugar factories. Potatoes play but little part in the industry. 3,000 industrial distilleries exist in France, and a very great number of small "farmer distilleries" (300,000).

Germany in 1908-09 produced 4,255,100 hl. (100 per cent.) of alcohol, as shown in following table:—

3,419,200 hl.	from	potatoes (from 6,400 "farmer" distilleries).
408,900	,,	grain (from 730 *industrial* distilleries and compressed yeast manufacturers).
291,700	,,	grain in 6,600 "farmer" distilleries.
86,800	,,	molasses (27 molasses distilleries).
48,500	,,	fruit (apples, etc.), wine, yeast, etc., in 60,000 very small distilleries.
Total 4,255,100	in	74,000 distilleries.

As raw products, nearly 3,000,000 tons of potatoes, 293,000 tons of grain (rye, barley, maize), and 32,000 tons of molasses are used. Contrary to France, in Germany little spirit is produced from sugar beet or molasses. This was a consequence of the taxing of the mash capacity of the vats, which made the economic working of their mashes impossible. Since the vat tax (in 1909) has now been abolished, we may expect shortly to see in Germany a great increase in the amount of alcohol produced from sugar beet and molasses.

Of the total amount of German alcohol produced, 2,651,000 hl. (4.2 l. per head) is consumed as a beverage, and 1,480,000 (2.3 l. per head) for industrial purposes. 175,600 hl. (100 per cent.) were consumed in the manufacture of vinegar, but the bulk of the industrial alcohol is used for burning purposes, spirit lamps, etc.

Taxation of Alcohol

Distilled spirits when used as a beverage are subjected to very high taxation in all civilised countries, the taxation so greatly exceeding the cost of production that the whole industry is more or less completely dependent upon the particular excise laws of each country. In **England** (1909) a spirit duty of 11s. per gallon of proof spirit is levied; the cost of production being only about 1s. 6d. per gallon. The revenue derived from this source in 1908-09 amounted to £17,456,366.

The number of distilleries at work throughout the United Kingdom in 1909 was 166 (England 8, Scotland 132, Ireland 26). The number of proof gallons retained for consumption in the United Kingdom was (1908-09) 32,000,000. In **Germany** the excise was until 1909 levied on the capacity of the fermenting vats, and consequently the German distillers work with as concentrated mashes as possible, up to 22°-25° Brix. In 1909 this mode of taxing the capacity of the vats ceased, and so the character of the German distilleries may be expected to alter considerably in the near future. A duty of 105-125 m. per hectolitre is now levied (1910), the exact amount of duty varying with the *maximum* amount of alcohol given by each distiller every ten years—the larger the production the larger the tax. An additional tax of 4-14 m. protects the small "farmer distilleries" against the large industrial concerns—the larger the distillery the greater the tax. In 1910-11 in

* 1 hectolitre = 100 litres = 22.01 gallons.

Germany the amount of spirits retained for consumption amounted to 1,780,000 hl. (2.7 l. per head). The duty levied on imported spirits is 275-300 m. per 1 dz.* The total revenue raised in Germany by the spirit duty amounted in 1908-09 to 162,700,000 m. The cost of manufacture of 1 hl. of alcohol (100 per cent.) is 25-30 m. The selling price of the taxed fine alcohol is 150-175 m. per hectolitre. In the **United States** the number of distilleries operated is about 1,800. The capital invested in distilleries and the production of potable spirits amounted to $50,101,000 in 1904, and to $72,450,000 in 1909 (increase, 45 per cent.). The value of the products increased from $131,270,000 (1904) to $204,699,000 (1909). The import of distilled spirits amounted in 1910 to $7,228,000, on which a duty of $9,116,000 was raised (126.12 per cent.).

Denatured Alcohol

Alcohol for industrial purposes† is now duty free in most countries including England. The tax on such alcohol for many years most injuriously affected the industry in fine chemicals in England. To such alcohol, however, substances must be added so as to make it undrinkable. The substances added must be of such a nature as to render their removal very difficult by simple operations. In England **completely denatured alcohol** (mineralised methylated spirit) is made by adding 1 part of wood naphtha to 9 parts of grain alcohol (50 per cent. *above* proof), and to the mixture 0.385 per cent. of mineral naphtha (petroleum of sp. gr. not less than 0.800). In the **U.S.** the denaturing mixture is ½ vol. benzine + 10 vols. methyl alcohol to 100 vols. ethyl alcohol. Completely denatured alcohol is allowed to be sold only by licensed retailers for general use (but not for making beverages or medicines).

Incompletely denatured alcohol (industrial **methylated spirits**) consists of not less than 5 per cent. of approved wood naphtha or other substance or combination of substances approved of by the Commissioners of Customs and Excise.

The wood naphtha used must be so impure as to render undrinkable alcohol to which it has been added. It must contain *not less* than 72 per cent. by vol. of methyl alcohol, and not *more* than 12 g. per 100 c.c. of aldehyde, acetone and ketones (estimated by Messinger's iodoform process as acetone) nor *more than* 3 g. of esters (estimated as methyl acetate by hydrolysis). At least 5 c.c. of N/10 acid must be necessary to neutralise 25 c.c. of the naphtha; not more than 30 c.c. of the naphtha should decolorise 0.5 g. of bromine in aqueous solution.

Industrial methylated spirits can only be purchased for manufacturing operations from a methylator. **Specially** denatured alcohol, suitable for particular industries, is allowed in cases where the presence of the above-mentioned denaturants would be injurious. The United Kingdom produced in 1908-09 of **industrial methylated spirit**, 3,884,740 proof gals. and 2,395,306 gals. of **mineralised methylated spirit**.

In **Germany** the usual denaturing agents for ordinary alcohol used for burning purposes is 2 per cent. by volume of wood spirit + ½ per cent. by volume of pyridine bases; or a mixture of benzol and light petroleum. In alcohol used for the manufacture of acetic acid the addition of acetic acid is allowed as a denaturant. Alcohol used for the manufacture of **ether** and **collodium** is denatured with 10 per cent. ether or camphor. To alcohol for varnishes ½ per cent. turpentine is added.

Benefits of Industrial Alcohol to Agriculture

Alcohol can be produced in practically unlimited quantities from a great variety of farm produce, so that every kind of soil and climate can be utilised. It can even be made from spoiled crops, corn stalks, refuse, etc. The alcohol so produced furnishes a cheap and excellent motive power of engines, and no doubt, after the exhaustion of the coal and oil supplies of the world, will be the ultimate fuel of mankind. For sunshine only is required for the production of the starchy materials from which alcohol is produced, and there is no exhaustion of the soil in the process. Only carbon, hydrogen, and oxygen are withdrawn from the air under the influence of sunlight, and, after the combustion of alcohol, they come back again as carbon dioxide and water. The nitrates, phosphates, lime, etc., absorbed from the soil by the growing vegetation, all remain in the immediate neighbourhood in the liquid wash from which the alcohol has been distilled off, and being used as fodder, are returned to the ground as manure.

In England and U.S.A. the bulk of the spirits produced is manufactured from grain. This was also the case in Germany one hundred years ago, but now, in that country, the bulk of the spirits is produced

* 1 dz. = 100 kilograms = $\frac{1}{10}$ ton.

† See *Journ. Soc. Chem. Ind.*, 1915, 34, 53.

from potatoes, which give a heavier and cheaper yield of starch per acre than any other vegetable and enable a very pure spirit to be easily obtained. In Germany, too, the manufacture of spirits is of very great benefit to agriculture, for it is carried on by the mutual co-operation of farmers, who sow their own potatoes and then cart them to a joint-owned distillery, where they are converted into alcohol in the winter months (up to May), while the spent wash and residues, rich in nitrogenous matters, is utilised as a cattle-food *on* the farms.

Consequently hand in hand with the production of alcohol there goes on an extensive breeding of cattle, which again produce the manure necessary for the continuous cultivation of crops. In 1906 no less than 71,000 of these so-called "farmer distilleries" were in operation. Besides these, however, were about 1,000 industrial distilleries, usually situated in or near a town, many of such distilleries specialising in the manufacture of yeast as described under that heading.

Four kinds of distilleries may be recognised :—

1. Those producing alcoholic beverages containing 25-60 per cent. of alcohol. In this class come the whisky and brandy manufacturers.

2. Those producing absolute alcohol up to 80-95 per cent., such alcohol being in too concentrated a form for drinking purposes. Under this heading may be classed the German potato distilleries, the great maize and molasses distilleries, and generally, manufacturers of industrial alcohol.

3. Alcohol rectifiers, where the crude 80-95 per cent. alcohol is redistilled and purified.

4. Compressed yeast manufacturers. In these distilleries the main object aimed at is the production of yeast, the spirits being produced as a by-product.

RAW MATERIALS USED IN THE PRODUCTION OF SPIRITS

Although alcohol can be obtained from the ethylene, C_2H_4, contained in coal gas, or directly from acetylene, C_2H_2, from calcium carbide, by means of concentrated sulphuric acid, yet in practice it is almost invariably obtained from sugar or starch, although attempts, attended with a certain amount of success, have been made to produce alcohol from wood cellulose. (See **Alcohol from Wood**, p. 294.)

The raw materials for the production of spirits may be divided into three great classes, as follows:—

1. **Alcohol-containing Materials.**—In France, Spain, Italy, and in fact all lands where wine is produced on a considerable scale, spirits are produced by distilling wines or wine lees. Such spirits are known as brandies, and are much valued on account of their pleasant aroma, due to wine fusel oils. Genuine **brandy** is obtained by distilling wine in small pot stills. The best brandies, called Cognacs (Charente and Charente Inférieure) from the districts in which they are made, are of a peculiarly fine and delicate character, and fetch 1,000 francs per hectolitre. They are made from light white wines possessing no marked bouquet. They are used for adding to champagne. The fuller and more aromatic wines of Burgundy and the Gironde do not yield such good brandies. A large amount of brandy is also made by adding water to wine lees (*i.e.*, the pulp of skins, pips, wine yeast, etc., remaining in the wine-press) and distilling. Artificial cognac oils (see p. 251) are largely manufactured for adding to cognacs. Brandies improve with age.

2. **Sugar-containing Materials.**—It is also possible to produce alcohol from sacchariferous substances, such as sugar beets, figs, amber cane, and especially the residual molasses from sugar manufacture. As these substances already contain sugar they do not need the mashing process necessary with starchy raw materials, and may therefore be ground up and directly fermented with yeast. France produces more than one-third of her spirits from the fermented juice of the sugar beet. In Portugal the carob bean (St John's Bread) is fermented and distilled, and in Brazil strawberries. In Jamaica and Cuba molasses and sugar-rich residues, such as cane-megasse, from the manufacture of cane sugar are allowed to spontaneously ferment, and then are distilled for **Rum**. Fictitious **rums**, however, are now made from alcohol flavoured with essential oils ("rum essence"). Rums contain 50-60 per cent. of alcohol, and sugar is often added. **Arrak** is produced in Java in a similar manner from the cane sugar and the sugar-rich juice of the sugar palm, which is allowed to ferment, either spontaneously or with the addition of certain rice yeasts.

Cherry brandy and **plum spirits** are produced by distilling fermented cherries or plums and contain oil of bitter almonds and a trace of hydrocyanic acid.

Gin is obtained by distilling plain spirit in the presence of flavouring agents, such as juniper, angelica, cinnamon, sweet fennel, coriander, etc. Flavouring agents are often added after distillation. Sweetened gin contains 3-6 per cent. of sugar.

In short, all sweet fruit juices of kernel and other fruits (apples, pears, melons, figs, raspberries, strawberries, rowan berries, etc.), when mixed with sugar, and fermented and distilled, yield brandies of various aromas.

3. **Starch-containing Materials.**—Corn and potatoes form by far the most important alcohol-producing materials. In *England* most of the spirits are made from wheat, barley, and rice. Scotch whisky is made from malted barley. In

Germany nearly 80 per cent. of the total amount of spirits manufactured is made from **potatoes**, the remainder being made from wheat, rye, and maize, with the simultaneous production of compressed yeast. In *France* beet molasses and wine form the principal source of spirits, potatoes and corn contributing little to the total amount manufactured. *Hungary* and the *United States* make a large amount of spirits from **maize**, and *Russia* from rye. The use of potatoes, however, is extending in these lands, especially in Hungary and Russia—nearly half the spirits produced by the latter country now being manufactured from potatoes.

In hot countries a potato (sweet potato, Carolina potato), which also contains, besides starch, a considerable amount of sugar, is an important raw material for the manufacture of spirits. It is cultivated in Brazil, the West Indies, the Azores, Algiers, etc. etc.

Potatoes contain 16-24 per cent. starch, 1.95 per cent. nitrogenous substance, and 75 per cent. water. Recently potatoes have been put on the market in a dried powdered form. 100 parts of dry potatoes contain: Starchy matter, 70-78 per cent.; protein, 6 per cent.; water, 9-18 per cent. **Maize** contains on the average: Starch, 68 per cent.; moisture, 13 per cent.; protein, 10 per cent. **Wheat** contains 50-70 per cent. starch, and 7-21 per cent. protein. **Oats** contain 58 per cent. starch, 10 per cent. protein. **Rye** contains 68 per cent. starch, 11 per cent. protein.

THE MANUFACTURE OF SPIRITS

In a grain or potato distillery three and sometimes four main operations take place, namely:—

1. **Mashing**, *i.e.*, the conversion of starch into sugar by means of specially prepared malt.
2. **Fermenting** and **yeast production.**
3. **Distillation of the alcohol**; and, sometimes,
4. **Refining the alcohol by redistillation.**

In brandy and molasses distilleries the mashing process and malt preparation is unnecessary. Only the fermenting (2) and distillation (3) takes place.

The main operations of the brewer and distiller are identical in that both convert starch into sugar by means of diastase, and sugar into alcohol by means of yeast. But otherwise the method of operation in the two cases differs considerably. Thus the brewer seeks to produce **beer** which contains only a small amount of alcohol and has other constituents, such as the dextrines, flavouring principles, etc., of equal importance. He does not, therefore, completely convert his starch into maltose, otherwise a very thin beer, lacking body and palate, would result. But the distiller's object is to produce **alcohol** as such, and with this aim in view he carries his fermentation as far as possible, converting as much as possible of his starch into sugars, avoiding the formation of dextrines and fermenting these into alcohol.

The colour of the grain and the nature of the husk—which are of vital importance for the production of a palatable beer—matter little to the distiller, provided only that the grain is sound, contains a high percentage of starch and nitrogenous matter—the latter being necessary because much nitrogen-rich diastase must be produced.

Barley intended for distillers' malt is cleaned, graded, and steeped for a period ranging from two to four days, a somewhat longer period than is usual for brewing barley. The steeping water is usually liberally treated with antiseptics (bisulphite, lime, etc.) to prevent the development of bacteria which may subsequently injure the fermentation. The brewer has no necessity to use antiseptics at this stage, as any such bacteria, if developed, are later destroyed when the wort is boiled and hopped. The distiller, however, cannot boil or hop his wort and so must take every precaution at these early stages to avoid bacterial infection. The danger is especially great when maize is used for malting.

Malting Operations.—In **Scots pot-still whisky** distilleries, where nothing is used except barley malt, the process of malting is carried out as in brewing (which see), the flooring period, however, being slightly longer. In grain and potato distilleries, however, barley malt is used *not so much* as a source of alcohol as a source of the **diastase** to convert the starch of the grain or potatoes used in bulk for starch. Consequently in such distilleries the malt is grown in such a way as to contain a *maximum* of diastase. This, as the researches of Hayduck have shown, is attained by allowing the malt to germinate on the floor for a twenty-day period (in contradistinction to the brewing period of seven to ten days—"short malt"), since the mass of the diastase increases greatly with the progress of the growth of the malt. Such malt is known as "Long Malt," the seven to ten day malt used in brewing being known as "Short Malt." It is obvious that the longer the malt grows the greater will be the loss of starch (which is converted into CO_2 and sugars by the growing plant). In "Short Malt" the loss of starch amounts to about 6½ per cent. of the starch originally present, but in "Long Malt" the loss rises to 17 per cent. In other words, we obtain 100 parts of **short malt** for every 90 parts of **long malt**. Nevertheless, the 90 parts of the long malt contain as much **diastase** as 117-144 parts of short malt, so that in spite of the greater starch loss,

the preparation of long malt is of great advantage, enabling the distillers to effect a great saving in malt, sometimes as high as 50 per cent. Hayduck has shown that the relative diastatic strengths of **short** (seven to ten days) and **long** (twenty days) malt are:—

For heavy barleys 1 : 1.285.

For light barleys 1 : 1.605. (Hence the advantage of using small grain for distillers.)

Consequently the **long malt** process is employed in all modern distilleries. To produce it the grain is subjected to a lengthy steep until it absorbs 40-45 per cent. of water. It is then subjected to a very prolonged flooring of about twenty days at a moderate temperature (which should never exceed 63.5° F.). The development of mould fungi and bacteria is prevented by soaking the malt grain in dilute milk of lime (1 part of lime : 100 parts barley).

In contradistinction to the brewer, the distiller prefers **green** malt rather than **kilned** malt, because green malt possesses about twice the diastatic strength of kilned malt; the distiller regards his malt merely as an agent for saccharifying his starch and consequently will use as little kilned malt as possible. To the brewer, however, too much diastase is a positive disadvantage, as he does not want to completely convert all his starch to sugar, and the process of kilning is necessary to restrict the diastatic power of the malt and impart flavour to the beer. It should be noted, however, that the malt whisky distiller relies to a great extent on the kilning process for the development of the peculiar flavour of Scotch or Irish whisky, and consequently can only make a limited use of green malt. Also compressed yeast distilleries find that a certain proportion of kilned malt is necessary. Indeed, in hot weather it is often difficult to obtain a good supply of green malt as it will not bear carriage for any distance. Hence when the distiller finds himself unable to use green malt, he resorts to a malt which has been kilned at the lowest possible temperature.

Other Kinds of Malt

The diastatic power of malt made from various kinds of corn is given in the following table:—

Barley malt	1.00
Oat malt	0.30
Maize malt	0.28
Rye malt	0.93
Wheat malt	1.08

Wheat malt is too costly for general use.

In spite of the low starch-transforming power of oat malt, it is used on a considerable scale, usually mixed with barley malt, because the zymase content of the yeast is considerably increased by the addition of the oat malt, and it acts very rapidly in the mash-tun. Maize malt is used for spirit manufacture in countries where barley is expensive. Rye is malted with barley or oats.

Diastase from Fungi—The Amylo Process.—In large corn distilleries in France, Belgium, and Hungary utilisation is made on a large scale of the diastase-secreting fungus, *Amylomyces Rouxii*, instead of malt. A sterilised corn (usually maize) mash contained in a closed vessel is inoculated with a very small quantity—one-tenth of a gram is sufficient—and filtered air is blown through the fluid for twenty hours. The mould develops very rapidly and converts the starch. Then pure yeast culture is added, and fermentation proceeds on ordinary lines. Although the mould is itself capable of fermenting the sugar itself, the yeast acts more rapidly and gives a greater percentage of alcohol. Hence both act together, the mould transforming the starch into sugar and the yeast and sugar into alcohol. One gram of culture transforms 25 tons of corn, and saves 3 tons of malt and 1 ton of starch used in the malting. Moreover, the mash is sterilised and worked in closed vessels, so that undesirable bacteria, etc, cannot develop—which is a great advantage. Technical difficulties have prevented the application of the mould to working potato starch. Another mould fungus, *Eurotium oryzæ*, from Japan, saccharises starch exactly like malt. It contains diastase, which can be extracted with water and added to the mash to be converted (see pp. 226, 249).

Theory of Mashing for Spirits

The brewer does not seek to completely transform all his starch into sugar. He must have in his wort a certain proportion of dextrine and similar non-ferment-

able carbohydrates, otherwise his beer will be thin and poor. Moreover his wort, before fermenting with yeast, is hopped and then sterilised by boiling. Quite otherwise is it with the distiller. He desires to convert his starch *entirely* into fermentable sugars (to obtain a maximum yield of alcohol), and he cannot sterilise the wort so obtained by boiling before adding the yeast for the following reasons. In the first place mashing should be carried out at low temperatures in order to allow the diastase to act more powerfully than in the case of brewers' wash, and in the second place the diastase is allowed to act during the period of alcoholic fermentation. If the wort were boiled before adding the yeast the diastase would be destroyed (as it is in brewing), and so the diastase could not act during the period of alcoholic fermentation, and a large proportion (as in brewing) of the starchy carbohydrates would remain in an unfermentable condition. It must be understood that low-temperature mashing will not alone completely transform starch into fermentable sugars, being converted into dextrines which are not further converted by diastase alone, but require the combined action of **yeast** and **diastase** to break them down completely into fermentable sugars. Hence it is that the distiller cannot boil his wort, and so sterilise it (as in brewing), because he would completely destroy his diastase. This puts the distiller in a very disadvantageous position as compared to the brewer, as unsterilised wort forms an excellent medium for the growth of undesirable bacteria. He must therefore forego the full advantage of low-temperature mashing and heat the mash to a temperature which is unfavourable to the development of bacteria. He first heats the mash very rapidly to 130° F., when maximum saccharifying action takes place, and keeps it at this temperature for a little time. Then he heats rapidly to 144° F., when the maximum liquefaction of the starch takes place, and finally he heats to 150°-154° F., when most of the undesirable bacteria, etc., are destroyed, while the diastase is not seriously injured in the presence of the large amount of sugar which has been formed, since Delbrück and Pätzold have shown that diastase in solutions rich in sugar can withstand a temperature as high as 154° F. without being very much weakened, while in a very weak sugar solution it is seriously injured at 146°.

Preparation of the Mash.—In the manufacture of whisky and other grain spirits, as carried on in the United Kingdom, the mashing apparatus is very similar to that used for brewing. The starchy matter, however, is more thoroughly extracted than is desirable in brewing by making several (Scotland, three; Ireland, two) successive mashings with the ground malt, the liquor from the last mash being used for mashing the next lot of malt.

In potato and maize distilleries, however, the mashes are made on a different principle; their starch must be gelatinised by steaming, and malt is only used as a source of diastase for converting the starch into sugar, and not as a source of starch. 100 parts of potatoes require 4-5 parts of green malt, while 100 parts of maize require 9-10 parts of green malt. Usually a small malting is run in connection with the distillery in order to produce the green malt fresh as required, since it will not keep.

The potatoes are washed and placed in a conical shaped boiler, known as a Henze steamer or "High Pressure Converter." This contains at its upper end a manhole for charging with potatoes, and steam pipes, carrying high-pressure steam, are supplied at the top, sides, and bottom. The apparatus is also supplied with an air-cock at the top, water-cock at the bottom, and a blow-out valve at the bottom, whereby the potato wash is blown into the fermentation vats. The apparatus is charged with potatoes and nearly filled with water. Steam is then allowed to enter through the upper inlet pipe, the air-cock and lower water-cock being left open until all the air is displaced and much of the condensed water has run off. The air-cocks and water-cocks are now closed and steaming continued until the internal pressure has risen to 2 atmospheres, the water-cock being opened from time to time to allow the condensed and amniotic water to run off—the last drawn amniotic water contains starch and is run into a preparatory wash vat. The upper steam

valve is now closed and steam driven in through the lower inlet pipe until the pressure reaches 3-4 atmospheres; the apparatus is kept at this pressure for ten to fifteen minutes, then the lower steam inlet pipe is closed, while the upper inlet and blow-out valves are opened and the apparatus blown out. The sudden release of the pressure causes the superheated water and steam in the potatoes to explosively expand, and reduces them to a mash in which the starch is (all but 2 per cent.) completely gelatinised and dissolved. The blowing out lasts forty-five

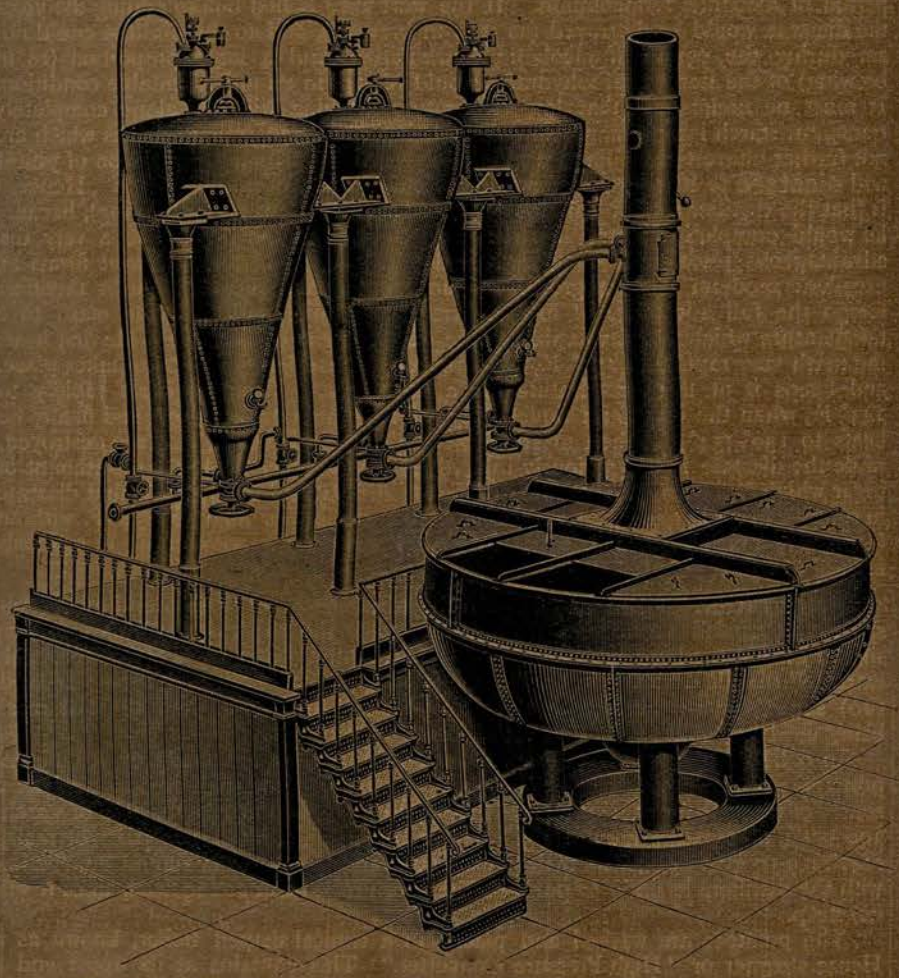


FIG. 122.—High-Pressure Converter or Steam Cookers (Henze Steamer) with Mashing Vats for Potatoes, etc. Llewellins & James, Bristol.)

to fifty minutes, the potato mash being forcibly driven through the conical end of the boiler into the mashing vat.

When the maize is to be treated, the whole corns are fed into the converter or Henze boiler with the addition of some water and steamed three hours at 3-3½ atmospheres. The mass must be continually stirred, and this is achieved either by a stirring apparatus or by blowing in steam tangentially through a number of holes in the body of the apparatus. Just before blowing out the pressure is increased to 4 atmospheres and the contents blown forcibly out at the bottom of

the boiler through the blow-out pipe, which is provided with a grating and a comminuting valve consisting of a cone-shaped tube with sharp screw edges and corners. The mass is blown forcibly against the sharp corners and the corns are smashed up, while the superheated steam and water in the corn grains, suddenly expanding under the reduced pressure, blow the grains into a pulp and gelatinise their contained starch. This treatment completely disintegrates maize. Since at these high temperatures and pressures carbohydrates begin to decompose and turn brown, *Mandl* steams **ground** maize in an open Henze steamer, and then blows out with compressed air at 4-5 atmospheres. The mash is quite white.

The mashing and cooling vat (Fig. 124) consists of a stout iron vessel provided with a powerful screw at the bottom and a cooling system of copper pipes, through which cold water is driven. The hot mash pouring into the vessel is hurled by the screw against the sides and cooling pipes and is rapidly cooled to the proper temperature. The apparatus is furnished with a funnel provided with an exhauster in the form of a steam jet situated in the funnel. This causes a rapid evaporation and consequent cooling of the hot mash, and also accelerates the rate at which the hot mass pours out of the steamer into the vat. The condensed water from the jet runs off through a pipe.

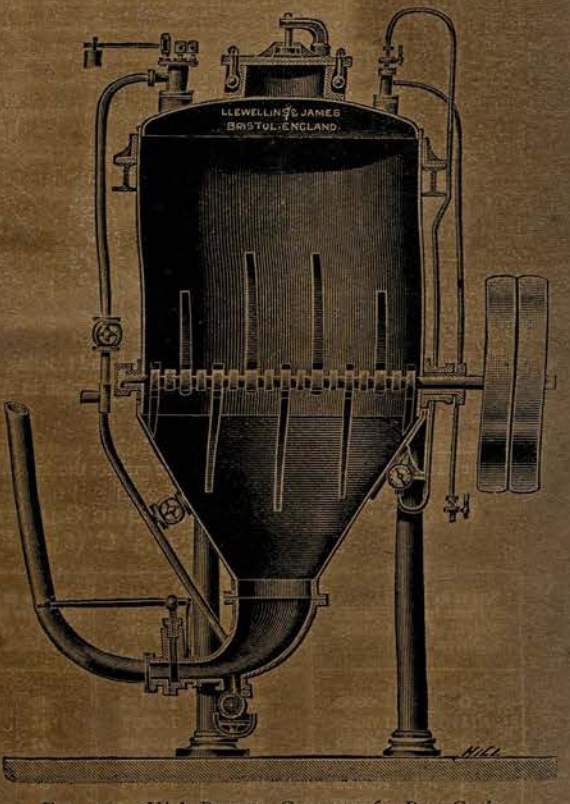


FIG. 123.—High-Pressure Converter for Raw Grain.

The method of mashing is as follows:—

The calculated amount of finely ground malt for the saccharisation of the mash is placed in the mash vat with a little water, and while the mass is thoroughly agitated the hot mash from the Henze steamer is slowly blown into the vat. The blowing out is regulated by the exhauster and the amount of cooling water, so that the temperature of the mash in this operation is maintained at 130° F. About five-sixths of the contents of the Henze steamer are withdrawn at this temperature, when the diastase acts most powerfully and the greatest amount of sugar is formed. The mash is allowed to stand twenty to thirty minutes at this maximum saccharifying temperature, then the temperature is raised to 144° F. rapidly by running more of the hot mash with rapid stirring and cooling, and the temperature kept at this height for some little time. Here the maximum liquefaction of the starch takes place, while injurious germs are seriously weakened. Finally the rest of the mash is blown in rapidly and the temperature rapidly raised to 150°-154° F., when all undesirable germs are killed. The process of saccharisation is complete in less than one hour. The mashing is now completed so far as its first stage is concerned, and after cooling to the proper pitching temperature, will be ready for the addition of the yeast.

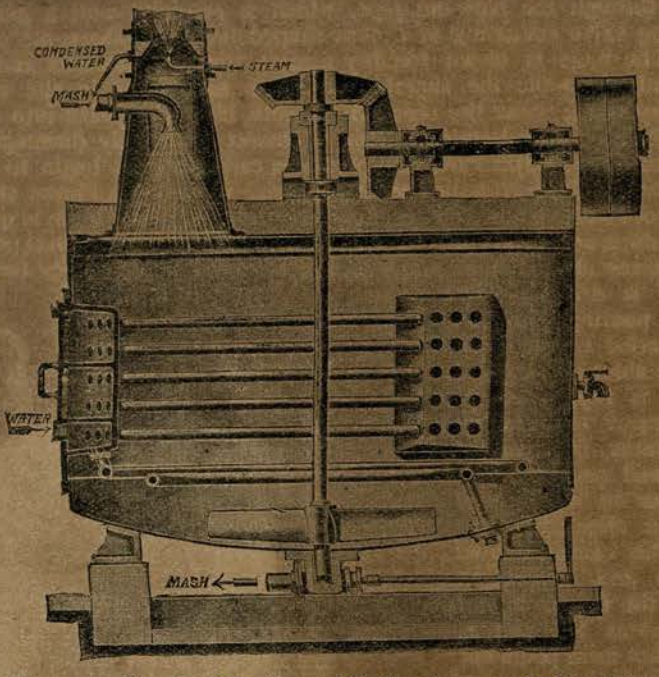


FIG. 124.—Centrifugal Mashing and Cooling Apparatus for Distilleries. (Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

Testing the Sweet Mash.—Sugar solutions possess higher specific gravities than water. The greater the proportion of sugar present the greater the specific gravity, as the following table shows:—

BALLING'S TABLE OF THE SPECIFIC GRAVITIES OF SUGAR SOLUTIONS AT 17.5° C. (63.5° F.)

Sugar in 100 Parts by Weight of Solution.	Specific Gravity.	Sugar in 100 Parts by Weight of Solution.	Specific Gravity.	Sugar in 100 Parts by Weight of Solution.	Specific Gravity.	Sugar in 100 Parts by Weight of Solution.	Specific Gravity.
0	1.0000	20	1.0832	40	1.1794	60	1.2900
1	1.0040	21	1.0877	41	1.1846	61	1.2959
2	1.0080	22	1.0922	42	1.1898	62	1.3019
3	1.0120	23	1.0967	43	1.1951	63	1.3079
4	1.0160	24	1.1013	44	1.2004	64	1.3139
5	1.0200	25	1.1059	45	1.2057	65	1.3199
6	1.0240	26	1.1106	46	1.2111	66	1.3260
7	1.0281	27	1.1153	47	1.2156	67	1.3321
8	1.0322	28	1.1200	48	1.2219	68	1.3383
9	1.0363	29	1.1247	49	1.2274	69	1.3445
10	1.0404	30	1.1295	50	1.2329	70	1.3507
11	1.0446	31	1.1343	51	1.2385	71	1.3570
12	1.0488	32	1.1391	52	1.2441	72	1.3633
13	1.0530	33	1.1440	53	1.2497	73	1.3696
14	1.0572	34	1.1490	54	1.2553	74	1.3760
15	1.0614	35	1.1540	55	1.2610	75.35	1.3824
16	1.0657	36	1.1590	56	1.2667		1.3847 = saturated sugar solution at 17.5° C. (63.5° F.)
17	1.0700	37	1.1641	57	1.2725		
18	1.0744	38	1.1692	58	1.2783		
19	1.0788	39	1.1743	59	1.2841		

Consequently, the determining of the specific gravity of the wort (by means of a hydrometer, called in this case a **saccharometer**) gives at once the approximate amount of sugar in the solution. Usually the percentage of sugar is directly marked off on the neck of the instrument, the values so obtained being known as "**degrees Balling**"—from the name of one of the introducers of the method into the distillery. In England and America **Bates'** saccharometer is largely used. The results are usually marked correct for a certain temperature (usually 17.5° C., or 63.5° F.), and the results for other temperatures are obtained by special tables.

Other tests applied to the sweet mash are:—

1. **Iodine solution** should produce no coloration. Any trace of starch present which has been unacted upon by the diastase would give a deep blue colour, and shows that the diastase is not working efficiently.

2. The presence of active diastase in the mash liquid, after the starch has been converted, is necessary for the after-fermentation. This is tested for by gelatinising 5 g. of starch with 200 c.c. water, cooling to 144° F. (62.3° C.), and adding 5 c.c. of mash liquid. The starch should be liquified almost instantaneously, and after thirty minutes iodine solution should not give a coloration with the liquid.

3. The acidity of mash is determined by titration with NaOH, so that the increase of acidity during fermentation may be known.

4. The amount of carbohydrates capable of fermentation is ascertained by inverting part of the filtered and diluted mash with HCl, neutralising, and estimating the sugars with Fehling's solution in the ordinary way.

Process of Fermentation.—Distillery yeasts work best at a temperature considerably above that most favourable to brewing types. If the distiller works at brewing temperatures brewing yeasts will predominate and these produce considerably less alcohol than proper distillery yeasts. 75°-81° F. are temperatures favourable for distillery yeasts, 60° F. for beer yeasts, and 40° F. for wild yeasts.

Distillery conditions of fermentation are very favourable to the development of bacteria (since distillers work with unsterilised wort and at high temperatures) which lower both the yield and the quality of the alcohol. The most dangerous of these are the butyric, mannitic, and mucic bacteria. These are suppressed by fermenting in a "soured" or acid wort and working at a high temperature. The acid usually used is lactic acid, but hydrofluoric acid is coming into use. A slightly acid wort favours the development of distillery yeasts, but checks brewery yeasts and bacteria. The souring is not carried out with the main wort, but a small mash (English "bub," German *Hefegut*) specially mashed at 148°-158° F. from kilned malt, to which is added unmalted wheat, maize, or rye. The potato mash itself has not enough yeast food for the vigorous propagation of yeast. This mash is heated to 122° F. (50° C.), and inoculated with a pure culture of lactic acid bacteria (sometimes the proper quantity of artificial lactic acid is added instead). At 122° F. they rapidly develop since no other bacteria appear capable of withstanding so well this high temperature in acid solution. When about 1 per cent. of lactic acid is present (determined by titration) the temperature is raised to 165° F. (73.9° C.) to kill the lactic acid bacteria and prevent souring proceeding in the main wort. The liquid is then cooled to 80° F. (26.7° C.), pitched with distillery yeast, cooled down very slowly with the attemperator to 60° F. (15.6° C.). The temperature then rises as fermentation proceeds, but must be kept under 85° F. Malt whisky distillers work at somewhat lower temperatures. Fermentation is forced as far as possible to convert all the sugar into alcohol.

Under these conditions practically only distillery yeasts thrive. Thus it has been shown that when a mixture of **brewery** and **distillery** yeasts have been applied three to four times to the sour wort, only pure distillery yeasts survive, the brewery yeasts having been killed.

Instead of lactic acid as the souring acid, a dilute solution of hydrofluoric acid has been used with great success, since the acid is poisonous to bacteria in an amount which does not affect distillery yeasts. Such yeasts can be acclimatised to stand 0.2 per cent. of the acid, a quantity which is quite fatal to any bacteria. Consequently, worts treated with hydrofluoric acid produce no side fermentation; while the acid, apparently, greatly stimulates the converting effect of the diastase, and thus permits low-mashing temperatures to be used.

The two distillery yeast races most widely employed and giving excellent results are **Species II.** and **XII.**, which have been produced by Lindner in the laboratories of the *Berlin Distillers' Association*. At the beginning of the season the

soured wort is pitched with the pure yeast culture, but as soon as this ripens and develops part is withdrawn and used as mother yeast for developing a fresh supply. Since in the distillery the danger of infection at high temperatures is very great it is necessary to frequently renew the supply of yeast.

Ten to fourteen hours after pitching the yeast has increased four to five fold, and the yeast is "**ripe.**" When this occurs it is run into the main or "sweet" wort and the fermentation begun as rapidly as possible, for if the yeast do not rapidly develop foreign bacteria will make their appearance. The initial temperatue is 68° F., but the temperature rises as fermentation proceeds. The chief period of fermentation occurs after twenty-four hours, decreasing again after twelve to eighteen hours. In this period of "after-fermentation" the diastase still present in the wort completes the conversion of any dextrine still present into maltose, which is then fermented by the yeast.

The temperature is kept during the whole fermentation under 86° (F. 30° C.) by means of a cooling coil (attemperator), for at higher temperature much alcohol is lost by evaporation and deleterious by-products are produced.

In Germany the worts are produced with as high a specific gravity as 1.110 ("Thick Mash") owing to the method of raising the duty, and a dilution of the mash with water towards the end of the fermentation acts very favourably by lowering the percentage of alcohol and CO_2, thus stimulating the yeast to a fresh degree of activity. In malt whisky distilleries the specific gravity of the wort is 1.050-1.060, but in grain distilleries the worts approximate the German gravity.

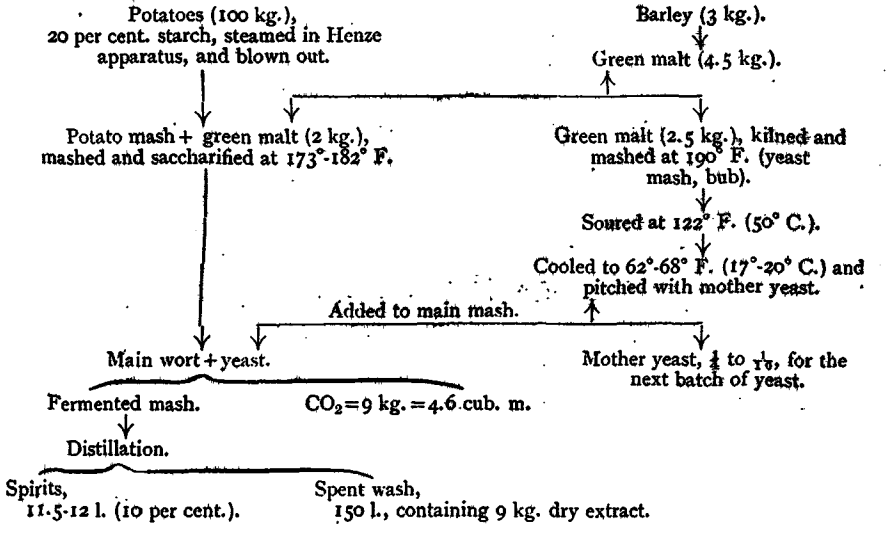
According to Maercker, concentrated mashes ferment more purely than thin mashes, and yield 12 or more per cent. of alcohol, which affords an excellent protection against injurious bacteria during fermentation. Moreover, they are more economical as regards time, cost, and work for producing a given amount of spirit than a thin mash.

In Germany the employment of thick potato mash is universal, because the mashing capacity is subject to taxation, and consequently the mashes are made as concentrated as possible in order to obtain the greatest possible yield of alcohol from the mashing capacity.

As a rule for thick mashes the fermenting vats have a capacity of 3,000-5,000 l. In the case of thin mashes and for molasses the fermenting vats have often a capacity of 40,000 l. Obviously the larger the vat the greater the amount of heat used for warming, etc., and for distilling the alcohol. It is usual to allow one-tenth of the fermenting vat clear for rising. Thick mashes in Germany contain 23-25 per cent. of sugar and dextrines. In corn distilleries the mashes contain 14-16 per cent. of sugar. In France and other countries where sugar beet and molasses are fermented the mashes often contain considerably less sugar than this.

In Germany the total time for fermenting is fixed by the custom officials at seventy-two hours.

The following scheme (after Ost) shows the chief operations in a German potato distillery:—


Potatoes (100 kg.), 20 per cent. starch, steamed in Henze apparatus, and blown out.
Barley (3 kg.).
Green malt (4.5 kg.).
Potato mash + green malt (2 kg.), mashed and saccharified at 173°-182° F.
Green malt (2.5 kg.), kilned and mashed at 190° F. (yeast mash, bub).
Soured at 122° F. (50° C.).
Cooled to 62°-68° F. (17°-20° C.) and pitched with mother yeast.
Added to main mash.
Main wort + yeast.
Mother yeast, ¼ to 1/10, for the next batch of yeast.
Fermented mash.
CO_2=9 kg.=4.6 cub. m.
Distillation.
Spirits, 11.5-12 l. (10 per cent.).
Spent wash, 150 l., containing 9 kg. dry extract.

Yield.—As a rule about 2 per cent. of starch remains in the skins, etc., of the potato or corn. Of the dissolved starch about 5 per cent. remains unfermented.

Further losses also occur during fermentation owing to the production of by-products such as lactic acid, acetic acid, succinic acid, glycerol, fusel oils, yeast cells, etc. Also a perceptible loss of alcohol through evaporation occurs. Consequently, although according to the equation $C_6H_{10}O_5 + H_2O = 2C_2H_5OH + 2CO_2$, 100 parts of starch are capable of yielding 71.6 l. of alcohol, in practice only 58 60 l. are obtained. 100 kg. of starch yield 46 kg. of CO_2 (= 24 cub. m.). This all escapes into the air as it is not economical to collect it.

Alcohol from Beet and Cane Sugar Molasses

Beet sugar molasses is somewhat difficult to ferment, firstly because it contains only a small amount of nitrogen and phosphorus for yeast foods, and secondly because of the presence of fatty acids and bacteria, which prevent the yeast from developing.

The method usually adopted for working up these residues is as follows: The alkaline molasses is mixed with two to three times its weight of water, just acidified with H_2SO_4 or HCl, and boiled in open vessels to sterilise the fluid and volatilise

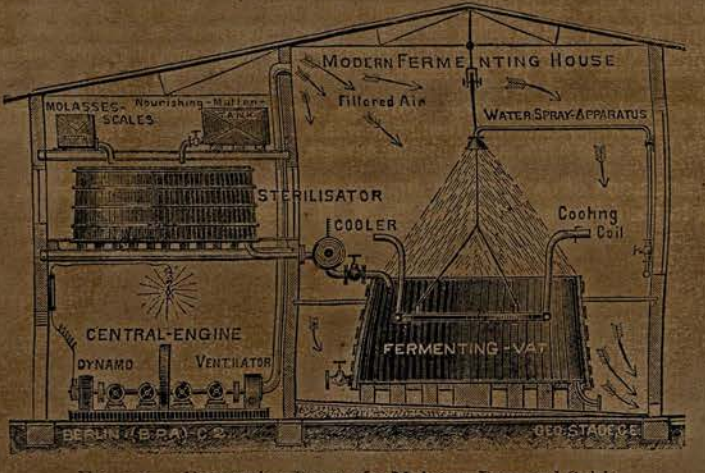


FIG. 125.—Fermenting Room of a Molasses Rum and Spirit Factory in Jamaica.
(Designed by George Stade, Berlin.)

some of the objectionable fatty acids, etc. The fluid now contains 15-17 per cent. of sugar, inverted by boiling with the acids and has sp. gr. 13° Bé. Solutions containing more sugar ferment badly. The mass is now cooled to 77° F. (25° C.), one-third is withdrawn and mixed with the yeast, and fermentation allowed to go on for some hours, when it is again returned to the main amount of molasses. The fermentation takes place quietly in large vats holding 200,000 to 400,000 l. and provided with cooling apparatus. The fermentation is usually incomplete, and a considerable amount of evil-smelling fusel oils are produced, but are separated from the crude spirit during the final distillation. Amine bases, formic acid, and aldehyde are present in crude molasses spirit.

Kraul & Wilkening confine their molasses in closed iron tanks of 400 hl. capacity, and cooled by a spray of water running over the exterior surface. This prevents the volatilisation of alcohol, and the CO_2 escaping from the vessels is pumped off, purified, and compressed into cylinders. The yeast used is bottom-fermentation beer yeasts, and the yield is 25,000 l. of alcohol (100 per cent.) and 1,800 kg. CO_2 per vat.

Geo. Stade of Berlin has effected several improvements in the manufacture of Jamaica rum from cane sugar molasses. A sketch of the fermenting room is shown. The rum ferment differs in structure from beer yeasts, having a maximum fermentative power at 30°-35° C. (86°-95° F.), is very sensitive to cold, and develops under special conditions into a mycelium.

The residues left after the fermentation of the molasses and distillation off of the alcohol are extraordinarily rich in **potash**, and contain nitrogen. The residues are evaporated dry, and used as manure, or they are worked up for potash, ammonia, and cyanogen compounds (see p. 376).

The calcined residues are known as calcinated vinasse (German *schlempekohle*), and contain 40-70 per cent. of potash salts. See under **Sugar**.

Alcohol from Wood

The production of alcohol directly from wood in an economical manner is one of the great industrial problems of the present time. 55-60 per cent. of wood is composed of cellulose, $(C_6H_{10}O_5)_n$ — a very complex carbohydrate — which, when treated with concentrated H_2SO_4, first dissolves to "amyloid," and then, after diluting with water until the solution contains 1-2 per cent. of acid, and heating to 120° C. under pressure, is readily transformed into dextrose, $C_6H_{12}O_6$—a fermentable sugar. In other processes, such as Simonsen's, the wood is directly heated with dilute H_2SO_4 under a great pressure, when it is transformed into dextrose. The solution is then neutralised and fermented. The disadvantage of these latter methods is, however, that the dextrose formed is partially destroyed again at the high temperatures and pressures employed, and consequently the yield of alcohol from cellulose sinks to 15 per cent., or from wood alone (sawdust, containing 55-60 per cent. cellulose) only 5-6 per cent. alcohol. Starch under similar conditions gives a far more abundant yield, 100 kg. starch giving 60 l. of alcohol (48 per cent. yield). In the manufacture of sulphite cellulose for paper from wood, to every ton of cellulose treated, nearly 10 tons of sulphite wash results, containing over 1 per cent. of fermentable sugar. In Sweden efforts have recently been made to utilise this waste fluid by neutralising with $CaCO_3$, fermenting with yeast, and distilling for spirit. 1,000 volumes of the wash yields 6 volumes of alcohol (100 per cent.), which contains a considerable amount of methyl alcohol, and may be used as methylated spirits. See **W. P. Cohoe**, "Hydrolysis of Sawdust," *Journ. Soc. Chem. Ind.*, 1912, 513.

Willstatter and Zechmeister (*Ber.*, 1913, 46, 2401-2412) completely convert cellulose into dextrose *at ordinary temperatures* by treating it with a strong solution of HCl gas in water (40-41 per cent. HCl) for 24-48 hours, a very notable advance.

The distillation of the alcoholic liquors, in order to obtain pure alcohol, is treated at length in the following article by Mr W. H. Stephens.

DISTILLATION OF ALCOHOLIC MASHES AND MODERN DISTILLING PLANT

LITERATURE RELATING TO DISTILLATION

Details of plant and methods used in distillation are given in the numerous works on spirits and industrial alcohol mentioned in the section on **Spirits** and industrial alcohol, p. 278. The following works specially deal with distillation and may be recommended :—

BARBET.—"La Rectification." Paris, 1895.
SOREL.—"La Distillation." Paris, 1898.
,, "La Rectification de l'Alcool." Paris, 1894.
HAUSBRAND.—"Die Wirkungsweise der Rectificier- und Destillir-Apparate." Berlin, 1893.

The most concentrated alcoholic mashes contain only 10-12 per cent. of alcohol, and to separate the alcohol in a concentrated form from the mash recourse must be had to distillation. Pure absolute alcohol boils at 78.3° C. (760 mm.), whereas water boils at 100° C.

Simple Distillation.—Certain classes of alcoholic beverages, *e.g.*, whisky, brandy, rum, etc., depend for their characteristic flavours on the retention of a considerable amount of volatile by-products of the wash. For this kind of product the simple stills are the best, since they do not effect the complete separation of the alcohol and the fusel oils, the presence of the latter being essential for giving a characteristic odour to the beverage. Such beverages contain 25-60 per cent. of alcohol.

Fig. 126 shows a simple still for brandy—A is the body of the still, C the head, and S the condensing worm, which is immersed in a tank of water. The spirit runs out through X and is received in a suitable receptacle.

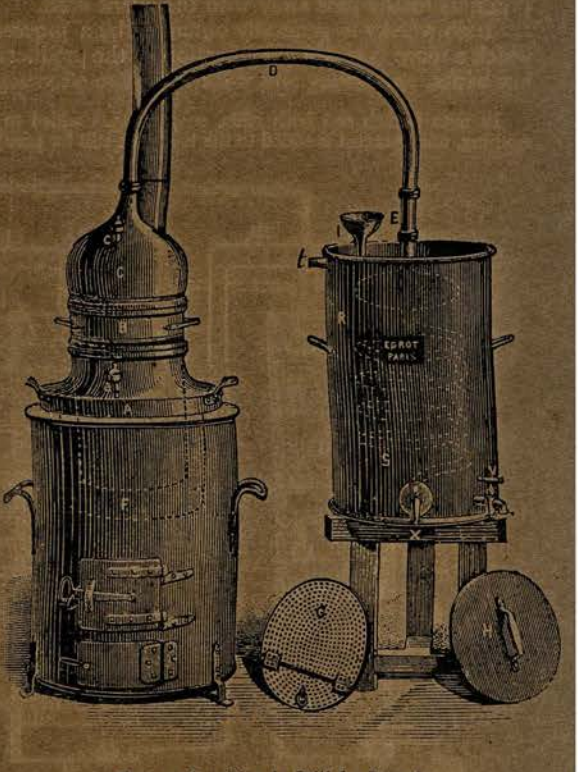


FIG. 126.—Simple Still for Brandy.
(Egrot, Paris.)

The pot stills of Scotch and Irish whisky manufactories are of this type, although larger, and usually set in masonry over a naked fire. Sometimes the stills are heat by steam jackets or steam pipes. The neck of the still is long; the rectifying

thus obtained is sometimes enhanced by the introduction of rectifying devices between the still and the condenser. The first distillate is richest in alcohol. When one-third to one-half of the wash has been distilled over the residue is "spent wash" free from alcohol. The distillate contains much water, and to raise the alcohol content it must be repeatedly distilled.

The following numbers suffice to give an idea of the results obtained with a simple still of this kind: 1,000 volumes of mash containing 10 per cent. of alcohol were distilled until 400 volumes passed over, this 400 volumes was again distilled and so on. The alcohol percentages in the resulting distillates is shown below:—

(1)	1,000	volumes	when	distilled	yielded	400	volumes	liquid	containing	25 per cent. of alcohol.
(2)	400	,,	,,	,,		200	,,	,,	50	,, ,,
(3)	200	,,	,,	,,		140	,,	,,	71	,, ,,
(4)	140	,,	,,	,,		125	,,	,,	80	,, ,,

Four separate distillations, therefore, were required to give a product containing 80 per cent. of alcohol and by repeated distillation it is possible to obtain a spirit of 96·97 per cent. alcohol. Further it is impossible to go; the remaining 3-4 per cent. of water must be withdrawn by dehydrating chemicals, such as lime or potash.

In making Scotch whisky two distillations are resorted to, the wash being distilled to yield a "low wine," which is again distilled. The final distillation is divided into three fractions: (1) foreshots, (2) finished whisky, (3) feints. The foreshots and feints comprise the various secondary products together with alcohol and added to the low wines for re-distillation. The less volatile portions of these by-products finally pass away with the spent wash.

Irish whisky is generally obtained by a process involving three distillations, in which a more complex classification of the products is effected, *e.g.*, strong and weak low wines, and strong and weak feints are often separated.

In both Scotch and Irish stills, soap is often added to the charge in the wash still to prevent frothing, and charcoal is added to the low wine still for purifying purposes.

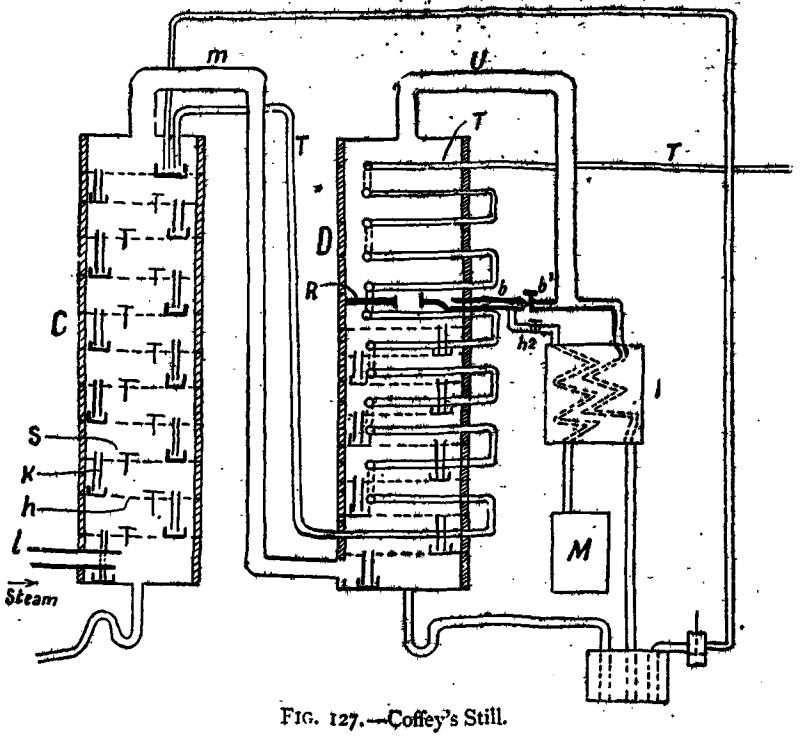


FIG. 127.—Coffey's Still.

Continuous Distillation.—The simple stills previously described do not remove the by-products except after repeated redistillations, and moreover the method of operation is discontinuous. Very early in the last century efforts were made to construct continuous stills which gave in a single operation a more concentrated spirit, and which removed to a great extent objectionable by-products. A still

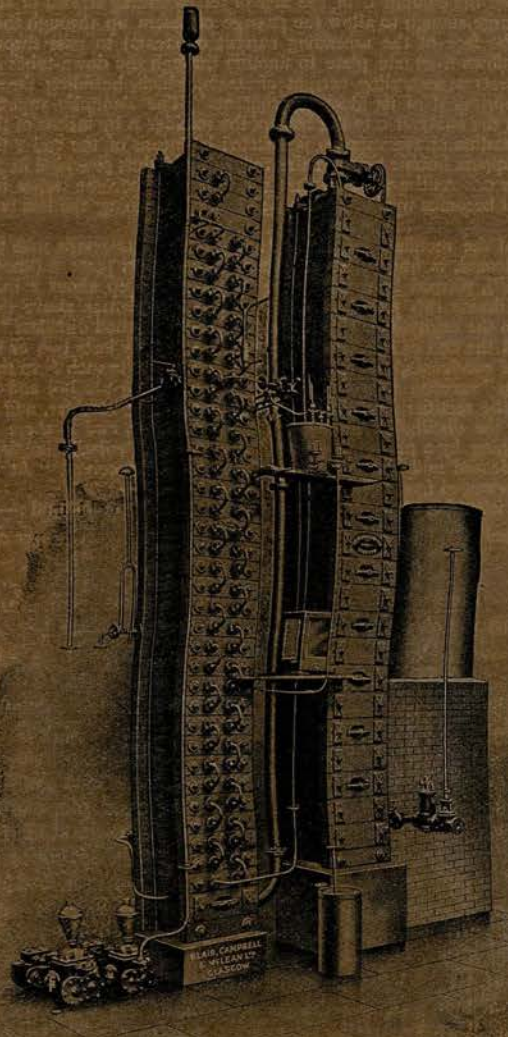


FIG. 127*a*.—Blair, Campbell, and M'Lean's form of Coffey's Still.

which has been largely used, and is still largely used, by British and Irish distillers, is the apparatus invented by Æneas Coffey in 1831, and shown in Figs. 127 and 127*a*.

This still comprises two columns, the analyser C and the rectifier D, which are divided into chambers made of wood and braced together in an iron frame. The chambers are separated by copper plates *h*, each having a large number of small perforations. Each plate has a safety-valve *s* and a drop pipe *k* standing with its upper end 1 in. above the plate and dipping into a cup

on the plate below. These overflows *k* are so arranged that the liquid flows across each plate, pursuing a zigzag course through the column.

In operation, steam is passed into the analyser C by a pipe *l* and passes from the top of the analyser to the base of the rectifier D by a pipe *m*. When the columns are filled with steam, the wash is pumped through a coil of piping T entering the top of the rectifier D and passing through each compartment in succession to the bottom (the wash being thus heated, and the surrounding vapours cooled) and is discharged on to the top plate of the analyser C. The wash, heated almost to boiling, now flows down the column C in the face of an ascending stream of steam. The small holes in the plate *h* are large enough to allow the passage of steam up through them, but too small to allow the wash (in the face of the ascending current of steam) to pass through. The wash, therefore, can only pour down from one plate to another through the down-tubes *k*. Consequently the downcoming wash meets an ascending current of steam, which, bubbling through each layer of liquid on the plates *h*, deprives it of its alcoholic contents. The alcoholic vapours and steam are led away from the top of the analyser C to the base of the rectifier D by means of the pipe *m*.

Here a partial condensation of the vapours is effected by means of the coil T through which the wash is flowing. The vapours bubble through the reflux liquid thus provided in precisely the same manner as in the analyser C. As the vapours pass upwards, they become richer in alcohol; as the liquid flows downward, it becomes weaker in alcohol, though retaining the less volatile constituent, namely, the fusel oils.

At a particular part of the rectifier, where the temperature corresponds with the temperature of condensation of strong alcohol, is fitted a stout unperforated copper plate R (known as the "spirit plate" or "dumb plate"), pierced by a wide pipe which stands up about 2 in. above the plate. A two-branched pipe *b* drains this plate. Normally alcohol condenses above this plate and runs through one branch b^2 to the refrigerator F and thence to the "finished distillate" receiver M.

At the beginning and the end of the distillation (which normally lasts two or three days without intermission) weak spirit condenses, and is run through the other branch b^1 to the refrigerator and thence to the "hot feints" receiver below. The liquid (containing alcohol and fusel oils) flowing away from the base of the rectifier also passes to the "hot feints" receiver, and is pumped thence continuously throughout the distillation to the top of the analyser, and is there re-distilled. The weak spirit vapours escaping by a pipe U, together with the more volatile impurities from the top of the rectifier, are condensed and also led to the "hot feints" receiver. At the end of each period the fusel oils are removed from the "hot feints" receiver.

W. E. Bell gives the following analysis of a sample of fusel oils so obtained:—

Amyl alcohol	42.2	per cent.
Butyl ,,	33.4	,,
Propyl ,,	18.9	,,
Ethyl ,,	5.5	,,

Ethyl esters of palmitic and oleic acids are also found in the "hot feints."

Fig. 127*a* shows a modern form of Coffey's still, as manufactured by Blair, Campbell, & M'Lean, of Glasgow.

Coffey's still has been described in great detail, not merely because it is the type in most common use in this country, but also because it affords a very valuable insight into the principles of continuous working. All continuous distilling plants comprise a continuous still, such as Coffey's analyser, and a continuous rectifier. Both the still and the rectifier are based on the same principle, namely, that by the repeated distillation and condensation that occurs in an apparatus in which a liquid and a vapour are flowing in opposite directions in intimate contact, the liquid is successively deprived of portions of its most volatile ingredients, and at the same time the vapour is successively deprived of portions of its least volatile ingredients, these being condensed and joining the down-flowing liquid, while the volatilised portions of the liquid pass on with the vapour. In the still, then, the wash enters at the top and meets a current of steam from below; the spent wash containing all the non-volatile ingredients and the major portion of the water passes out at the base, while the alcohol and volatile impurities together with water pass away at the top. In the rectifier, the vapours from the still enter at the base, while liquid provided by "dephlegmation," that is to say, condensation, flows downwardly; at the base, a liquid, comprising the major portion of the water together with fusel oils and small quantities of alcohol, flows away, while at the top the alcohol and the more volatile impurities (aldehydes, etc.) collect in the form of vapour and may be condensed.

These principles will be easily recognised as underlying the continuously-working distilling plants in use on the Continent.

The type most widely used is that designed by Savalle. Fig. 128 shows a typical Continental still of this kind:—

A is the distilling column, B the rectifier, C the dephlegmator (or condenser) and preheater for the wash, D the alcohol condenser, G the alcohol outlet, E the spent wash outlet.

The mash is forced through the pipe *s* into the dephlegmator C, wherein it is heated; then it passes in a hot condition through the pipe s_1 into the uppermost chamber of the distilling column A. The spent wash flows away through a regulator E. Steam enters by a perforated pipe *b* and

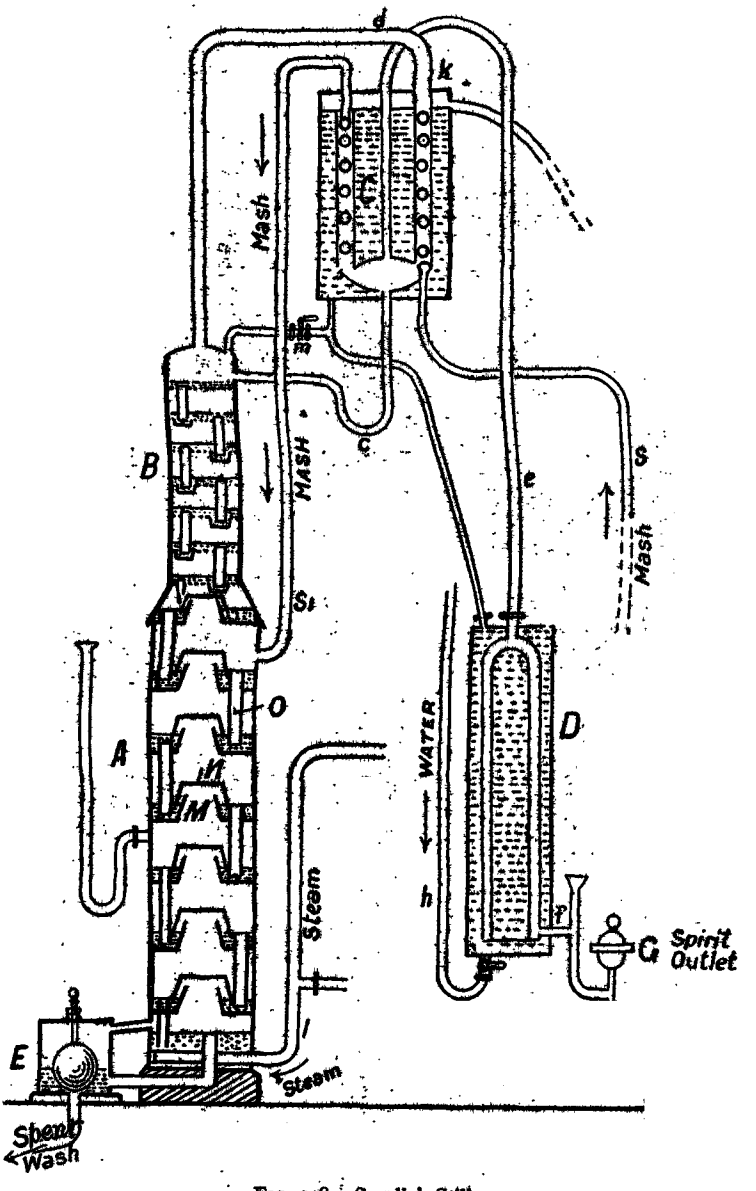


FIG. 128.—Savalle's Still.

vaporises the alcohol in the still A. The vapours enter the rectifier and pass away from the top by a pipe *d* to the dephlegmator C. The portions here condensed return by a pipe *c* to the rectifier. The remainder pass on to the spirit condenser by way of a pipe *e*.

The rectifying column B is composed of perforated plates of the same construction as Coffey's apparatus. The distilling column A is, however, of a different construction, and comprises plates

with central openings M surmounted by bells or hoods N, the lower edges of which dip below the surface of the liquid on the plates, which are provided with the usual overflow pipes O. The up-flowing vapours are thus caused to bubble through the liquid around the edges of the bells N (Fig. 128 and 129).

The dephlegmator shown consists of a tank filled with water. It contains a double-walled, annular vessel, through which the vapours pass, and which in its turn surrounds a copper worm through which the mash from the fermenting vat is pumped.

The main point in which this plant differs from Coffey's apparatus is that the dephlegmator and preheater for the wash C is entirely separated from the rectifier, no temperature exchange between the vapour undergoing rectification and the wash to be distilled being effected in the rectifier. It is the vapour from the top of the rectifier which exchanges heat with the wash, is thereby condensed, and returns by a pipe *c* to provide a reflux liquid in the rectifier. The column B is then a rectifier pure and simple. By this arrangement is obtained the advantage that the liquid which leaves the base of the rectifier must have been subjected to redistillation on all the stages of the column, whereas in the Coffey still some of the outflowing liquid may be derived from condensation in the lower part of the rectifier, and in consequence may not be satisfactorily freed from alcohol by redistillation.

A British still of this type is "Blair's" patent continuous steam working still, manufactured by Blair, Campbell, & M'Lean, Glasgow (Fig. 130).

It is obvious that the rectifying and distilling columns may be arranged side by side in the same manner as in Coffey's still. This arrangement has the advantage that the fusel oils may to a large extent be isolated and prevented from entering the distilling column. In modern plants for making industrial alcohol, it is not customary to pass the residue directly from the rectifier into the analyser in the manner described in connection with Coffey's apparatus. The oils are usually allowed to separate from this liquor, and are decanted off continuously, the liquid from which the oils have been removed being returned to the distilling column. Plants embodying this operation are described on pp. 306-311, under **Continuous Rectifying Apparatus and Combined Distillation Rectification Stills.**

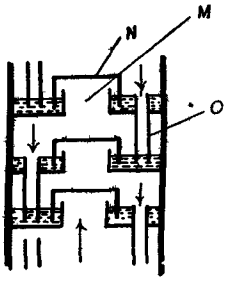


FIG. 129.

Rectification. — The various forms of distilling plant previously described do not provide alcohol sufficiently pure for industrial purposes. The raw spirit or phlegm contains a quantity of aldehyde and fusel oils. The operation of rectification is designed for the removal of these substances. In the older type of rectifying plant, as introduced by Savalle, for example, the spirit after dilution with 40-50 per cent. of water is rectified in a still consisting of a large iron boiler A (Fig. 2, p. 6) heated by steam, surmounted by a copper rectifying column B, 45 ft. often high, together with a dephlegmator C, from which liquid is returned to the rectifier by a pipe *m*, and a spirit condenser D. The operation is discontinuous, the boiler being filled with the diluted spirit and carefully distilled. The operation is then broken and the residues removed; then the boiler is refilled, and the distillation repeated. The loss amounts to 1.5-2 per cent. of alcohol.

The raw spirit was thus separated into four products, viz.: (1) **First runnings or foreshots**, which is a mixture of acetaldehyde and ethyl alcohol. It boils at a lower temperature than pure ethyl alcohol, and is called **ether** by the refiner. (2) **Clean or rectified spirit**, which is the intermediate product, and consists of almost pure alcohol, 96-97 volumes per cent. (3) **Feints**, a mixture of various alcohols, consisting of some ethyl alcohol and much amyl alcohol, and similar alcohols of high boiling points. (4) **Fusel oil**, which remains in the still together with the water.

Charcoal Filters.—The alcohol as it came from Coffey's and older stills contained anything between 80 and 90 per cent. of alcohol by volume, and always had a certain amount of fusel oil and aldehyde in it. These must be removed before the alcohol is fit for adding to good wines, liqueurs, etc., or can be used for many chemical purposes. It was therefore the custom to filter it through charcoal filters, which greatly improved its quality. Owing to the presence of absorbed oxygen in its pores the charcoal acts chemically on the higher alcohols, oxidising them to acids (also to

aldehydes), which then form esters with the excess of alcohol. Part of these esters are retained by the charcoal, but some remain in the spirit; consequently, although filtration through alcohol improves the taste and smell of the alcohol, it does not completely remove all the fusel oil. The charcoal, broken into lumps, is placed in a number of iron cylinders (which are sometimes 30 ft. high) arranged in series, and the spirit, after diluting to 50 per cent., is allowed to slowly flow

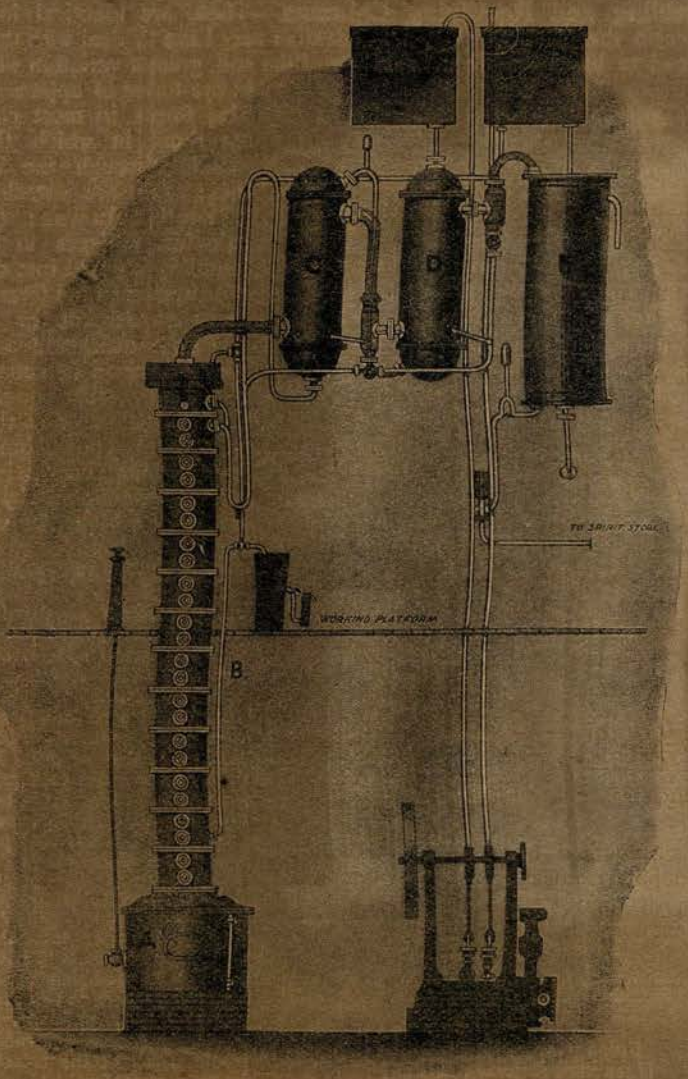


FIG. 130.—"Blair's" Patent Continuous Working Steam Still.

A, Still Kettle with Steam Coils; B, Analysing and Rectifying Column; C, D, Rectifying Wash Heaters; E, Condenser.

through them (Fig. 131). The last traces of alcohol are recovered by blowing steam through the charcoal, and it is regenerated by heating to redness in special furnaces.

Within recent years the expensive process of filtering through charcoal has been largely dispensed with, the distillers relying on carefully conducted rectification for the complete removal of the fusel oil and acetaldehyde, the former being now a valuable by-product (see pp. 312 and 383).

Before proceeding to a detailed description of more modern types of plant (including continuous apparatus for rectifying alcohol) it may be as well to note the different forms the various integers of the apparatus already described may take, and the additional devices which are essential to the efficiency of the apparatus.

Distilling and Rectifying Columns.—These are identical in principle, but since in the distilling column the distiller may have to deal with thick mashes which tend to block the various passages of the still, greater variation will be found in the forms of apparatus adopted. The forms in most common use are those in which the vapours bubble through the liquid, and these again are divisible into (1) "Plate" columns; (2) "Full" columns. Types in which the liquid is brought into contact with the vapours in the form of films or spray are also known.

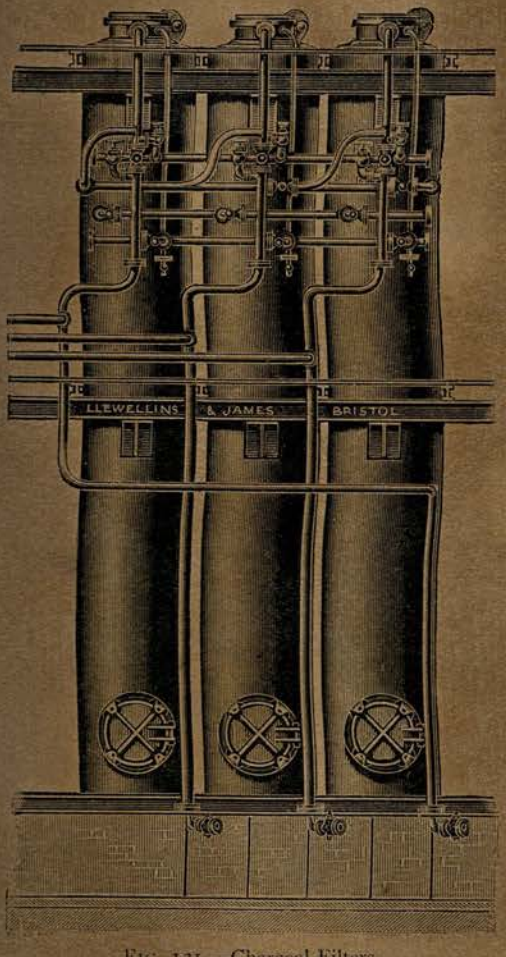


FIG. 131.—Charcoal Filters.
(Llewellins & James, Bristol.)

Plate columns are either of type described in connection with the Coffey still, comprising perforated plates, or of the type described in connection with the Savalle still, comprising large orifice surmounted by hoods by means of which the vapours are forced to bubble through the liquid (Figs. 128, 129).

An example of the form which a modern bubbling-hood plate takes is that used in Egrot's system, and shown in Fig. 132. This comprises a number of bells *k* arranged on a plate sloping towards the centre and provided with a number of partitions which force the liquid entering at *a* to follow a path *b c d e f g* which brings it past each of the bells before it reaches the exit *o*. In both types of plate columns we get, in each compartment, a layer of liquid and above it a stratum of vapour.

Guillaume's "inclined column" (Fig. 133) closely resembles the "plate" type, and was devised to meet the problem of thick mashes. It has, however, proved useful as a rectifying apparatus. This apparatus is made in two parts: the upper part of the casing is provided with depending partitions 3 extending across the whole width of the column, while the lower part is furnished with upstanding partitions *d*, alternately stopping short of either side of the casing. The liquid thus follows a zigzag course from top to bottom, as indicated by the arrows, while the vapours are forced to bubble under each of the partitions 3.

"Full" columns are, however, full of mash, the vapours passing from bottom to top continuously in bubble form. Obstructions cannot arise in this type of column, but unfortunately it is much less efficient than the "plate" type, and is therefore never used for rectifying purposes. The still used by Ilges, and shown in Fig. 134, is a good example of this type. It will be seen that the only internal fittings take the form of baffle plates *a*, *c*, which both lengthen and regularise the upward path of the vapours through the down-flowing liquid.

Of **Film types** two are worthy of mention, namely, those devised by Savalle and by Ilges.

Savalle's horizontal apparatus was devised primarily for dealing with thick mashes, and comprises a horizontal cylinder in which a number of discs partially immersed in liquid rotate on a horizontal shaft. The liquid flowing in one direction is thus continuously exposed in thin films to the action of the vapours flowing in the opposite direction. It is described in detail in British Patent 21,708, 1891.

Ilges and other inventors use a tower packed with glass balls or the like for rectifying purposes.

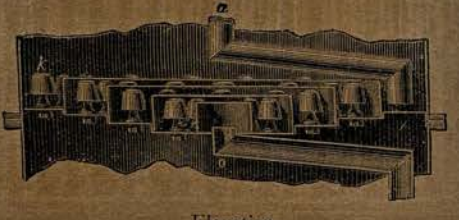
Spraying columns for distilling purposes have been devised by **Guillaume**; these are described in detail in British Patents, 3,561, 1903, and 11,475, 1906.

Dephlegmators.—A form of dephlegmator has been described on p. 300 in connection with Savalle's still. At one time it was thought that a dephlegmator such as that described had the effect of condensing from the vapours entering it a fraction containing the less volatile constituents, while allowing the more volatile constituents to pass on to the spirit condenser. According to this theory the dephlegmator thus had a rectifying or fractionating action. It cannot, however, be too strongly emphasised that the dephlegmators in common use, constructed as they are with cooling surfaces only, have practically no rectifying action, or, to use the words of Barbet, the condensed liquid has practically the same chemical composition as the mixture of vapours from which it is derived.

In France this principle has been largely recognised, and the evolution of distilling rectifying plant has followed lines entirely different from those based on the older theory.

Numbers of inventors—Ilges, for example, in Germany—working on the old theory and recognising that the dephlegmators in use were, from that point of view, highly inefficient, have improved their dephlegmators by combining with them constructions having a true rectifying action.

Plan.



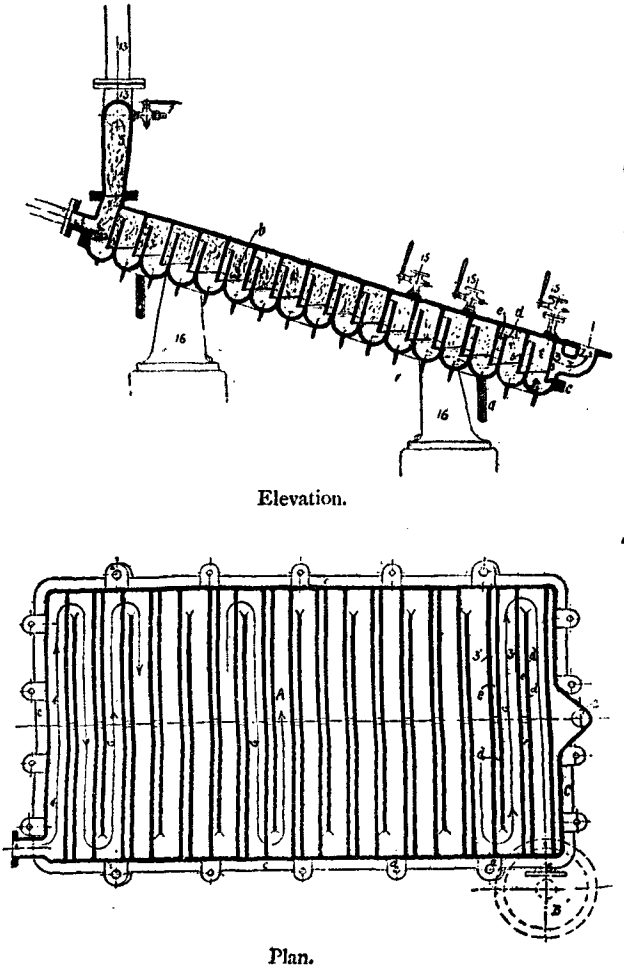
Elevation.

FIG. 132.—Egrot's Tray. (Egrot, Paris.)

An example of such a type of dephlegmator is sketched in Fig. 135, which was designed by J. Verchow, Germany, and is constructed by Schmidt & Son, Nauen, Mecklenburg, Germany. It consists of three casings placed one within the other; the middle casing on both its inner and outer sides, and the inner casing on its outer side only, are provided with annular angle flanges riveted in position. The mash is pumped into the apparatus through A, and flows in a gradual spiral path formed between the outer and middle casing by the flanges, until it reaches the outlet B, whence it pours into the mash or distilling column. The alcohol vapours from the distilling column enter the dephlegmator at C and pursue a spiral course upwards through the space G between the flanges upon the outer side of the inner casing and the inner side of the middle casing, a large portion condensing on the way and flowing down the spiral into the distilling head by G, the rest passing on and partially condensing in the cooling chamber situated in the upper part of the dephlegmator, whereas the uncondensed alcohol vapour passes out through D into a condenser where it is condensed and drawn off as pure alcohol. The alcoholic vapours condensing in the upper cooling chamber run through the tube cc and trickle down between the flanged castings into the upper part of the distilling column. The inner casing is filled with cooling water which completely surrounds the cooling chamber. The mash is heated by the warm outer wall of the middle casing and in its turn cools the alcohol vapours.

It is by the introduction of these flanged castings, which provide a long path in which the liquid is to some extent removed from the cooling action of the walls and is subjected to the action of the hot vapours, that the repeated redistillations which constitute the operation of rectification are alone rendered possible.

The Wagener type of dephlegmator is based on the same principle. Here will be seen cooling and condensing surfaces constituted by corrugated walls *d* and tubes *a*, Fig. 135. These have no rectifying action. These surfaces are, however, provided with metal strips *i* and *c*, which enable the vaporisation of the liquid by the hot vapours, and which perform the actual rectification.



Elevation.

Plan.

FIG. 133.—Guillaume's "Inclined" Column.

Apparatus fitted with dephlegmators, such as those described, yield with ease an alcohol of strength 89-92 per cent. by volume in place of the spirit of 80-87 per cent. strength obtained in plant not fitted with such apparatus.

Pasteurisation.—This operation is characteristic of the rectifying plant adopted in France. It is based on two principles:—

(1) A condenser as such has no rectifying action; that part of the vapours which is liquefied is of almost exactly the same composition as the part which is not liquefied, particularly when the alcoholic vapours are of high degree.

(2) If any plate of a column is charged with boiling liquid, and a vapour of the same temperature is made to bubble through that liquid, then of that vapour the portions which are more volatile than any portion of the liquid will pass on without being liquefied. The only change in the composition of the liquid and vapour which can take place is such that the vapour yields a portion of its less volatile constituents to the liquid, and the liquid yields a portion of its more volatile constituents to the vapour. Turning to Fig. 136 which shows the top of a rectifying column A surmounted by a condenser or dephlegmator E from which the condensed liquid is returned to the top plate B of the rectifier, we find that in conformity with the first mentioned principle that the liquid thus returned is of the same composition as the vapours entering the condenser E, and accordingly contains alcohol together with head-products (aldehydes and ethers) but that, in conformity with the second-mentioned principle, by the time that liquid has reached the third

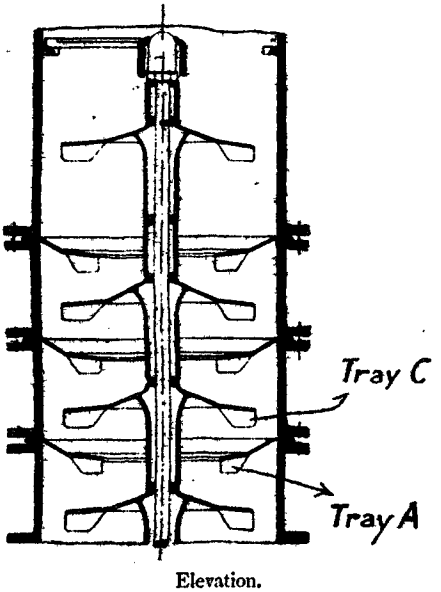
plate of the rectifier, those head-products have been volatilised, and that accordingly pure liquid alcohol may be withdrawn from that plate through a pipe H. This operation is that known as "Pasteurisation," and the resulting product is "pasteurised" alcohol. The vapours that escape condensation in the dephlegmator E pass to a condenser F, are there condensed to yield a liquid containing head-products which are subjected to further treatment.

Regulation.—To obtain absolutely uniform products, it is necessary to ensure that the amounts of the various distillates and of the residues leaving the base of the columns per unit time are constant and correspond exactly with the amount of free liquid entering the apparatus, and further, that the temperatures and the quantity of liquid in any part of the apparatus are also constant.

For example, the amount of steam admitted for heating purposes is controlled by a thermostatic device which responds instantly to any variation of the temperature in the distilling column.

While it is not intended to describe in detail the various devices used to ensure uniformity of working, it may be as well to consider the arrangements used in conjunction with the pasteurisation apparatus previously described with reference to Fig. 136. These will afford an insight into the scrupulous care that is necessary to obtain satisfactory results.

It will be remembered that the vapours pass from the rectifier A through



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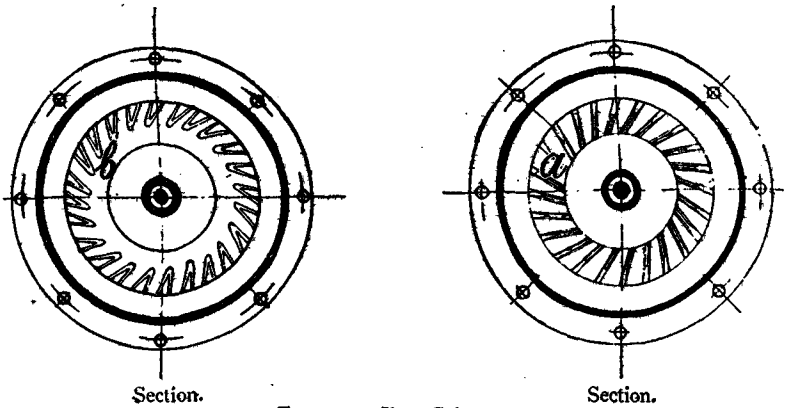


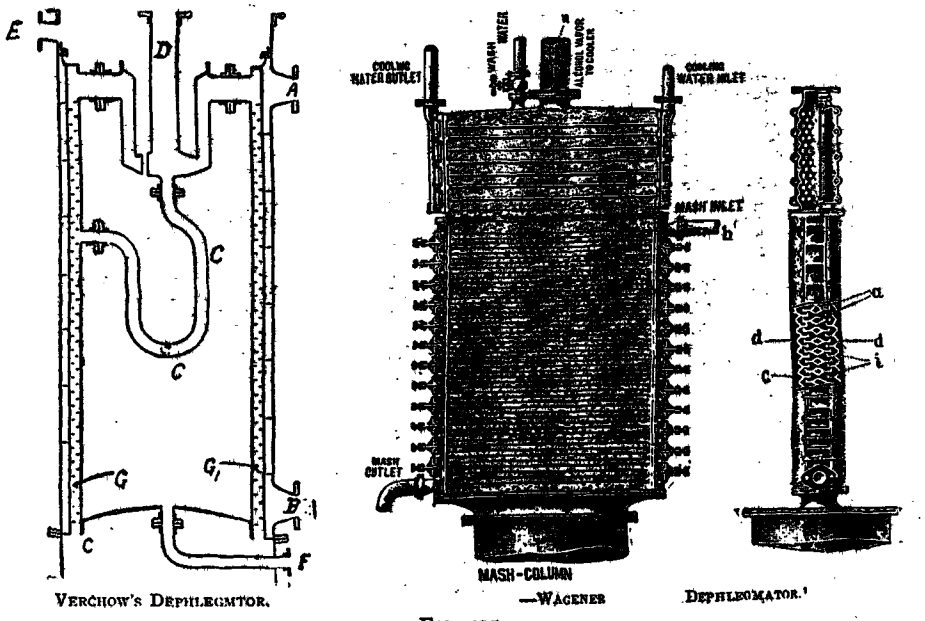
Section. Section.

FIG. 134.—Ilges Column.

the condensers E, F in succession. Pasteurised alcohol is extracted by a pipe H, is passed through a refrigerator G, and flows away through a test (or sight) glass P. Alcohol containing head-products flows away through a pipe L to a test-glass T. By means of cocks M and N the quantities of liquid flowing through the test-glasses are regulated to give outflows of pasteurised alcohol and alcohol containing head-products roughly in the proportion of 95 : 5. Suppose, then, that the condenser E does not condense its proper proportion of spirit. An excess over that flowing

away through the cock N will then be condensed in the condenser F. By the provision of a pipe R this excess is made to rejoin the spirit running from the condenser E to the top plate of the rectifier. To sum up, let us assume that by means of various other devices we have ensured that the rectifier is working uniformly in other respects so that vapour flows uniformly to the condenser E. We have a constant outflow through cocks M, N. Then by difference we shall have a constant excess of liquid, condensed in E and F, and not passing away through the cocks M, N. This will constitute the reflux or "retrogradation" in the rectifier A, passing steadily down the column from plate to plate to meet the constant upward flow of vapour.

Continuous Rectifying Apparatus.—As previously indicated, in rectification the manufacturer has to deal with "phlegms" or alcoholic liquids resulting from the distillation of various types of fermented washes, but all containing head-products (ethers and aldehydes), tail-products (fusel oils), and varying quantities of



VERCHOW'S DEPHLEGMTOR. DEPHLEGMATOR.

FIG. 135.

water. To get a continuous rectifying apparatus, it is then necessary to effect these operations in apparatus of the columnar type.

Barbet's apparatus is a typical solution of the problem (Fig. 137).

The phlegms (or raw spirit) are first treated for the removal of head-products. This is effected in a **purifying column**, A, to the upper part of which the phlegms are led from the preheater R. The column comprises essentially a distilling column surmounted by a short rectifying column together with the usual condensers B, C. The apparatus is worked in the same manner as an ordinary continuous still, but is so regulated that only about 5 per cent. of distillate is allowed to flow away through the test-glass P. This distillate comprises the most volatile ingredients—the head-products. The alcohol, purified in this manner, flows down to the base of the column A, and thence in the liquid form to the base of a rectifying column G. The rectifying column G also is constructed and worked on the general principles already laid down for continuous distillation. The most volatile ingredient—in this case, the alcohol—passes up the column in the form of vapour, and the less volatile ingredients—water and oils—pass downwards. In order to remove the last traces of head-products, the alcohol is condensed in H, K, and is pasteurised in the manner described on p. 304. The finished alcohol is extracted from the column G, and passes through a refrigerator E to the test-glass Q. Alcohol containing traces of head-products issues from the condenser K and passes away through the test-glass R.

The statement that the oils pass downwards with the water is, however, subject to a very important qualification. Duclaux has shown that the tail-products, though themselves less volatile than water, when mixed with water, boil at lower temperatures. Thus a 5 per cent. solution of butyl or amyl alcohol is more easily evaporated than a 5 per cent. solution of ethyl alcohol. In volatilising the whole of the alcohol in the phlegms, one cannot avoid volatilising the whole of the fusel oils. The liquid issuing from the base of the column G is, in consequence, water and nothing but water. The tail-products remain behind in the rectifying column, and if allowed to accumulate would gradually rise from plate to plate until in a continuous plant, such as that described, they would be found in the pasteurised alcohol. It is found that the tail-products accumulate on particular plates, usually the second and third plates below that on which the feed enters. By withdrawing from these plates a quantity of liquid (namely about 2.5 per cent.) such that the amount of oils thus removed is equal to the amount entering within the phlegms, the accumulation of the oils is prevented and the vitiation of the pasteurised alcohol with fusel is prevented. The oil-containing liquid is cooled in a cooler D and passes away through a test-glass T.

The apparatus also comprises steam regulators, and a device for testing the exhaustion of the phlegms, comprising a condenser and a test-glass, which should yield a liquid containing no alcohol. The exhausted phlegms from the base of the rectifier pass to the heat-exchanger R, to heat the incoming phlegms.

Apparatus of this type yield as finished alcohol about 91-92 per cent. of the alcoholic content of the phlegms from which it is derived.

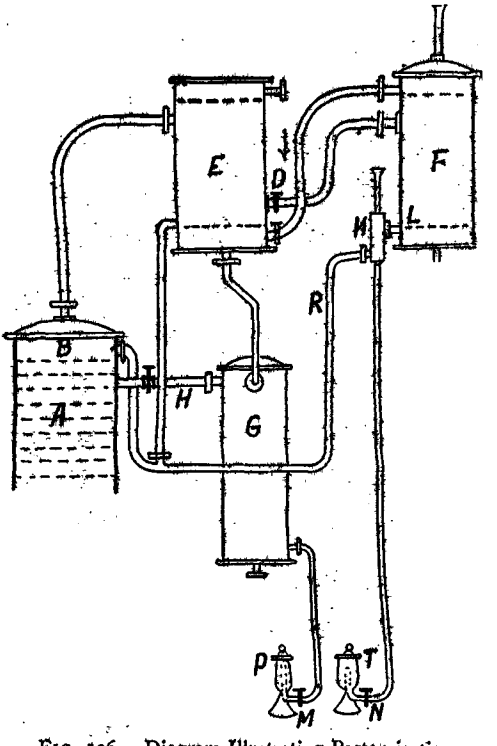


FIG. 136.—Diagram Illustrating Pasteurisation.

Combined Distillation and Rectification Stills.—Recently several firms have placed stills on the market which produce *directly* from the mash *at a single operation* a perfectly pure spirit at 96-98 per cent. alcoholic strength by volume, entirely free from fusel oil and aldehyde. These stills deliver continuously in four unbroken streams through four different orifices four different products, viz. :—

1. Pure **spirit**, 96-98 per cent. alcohol, comprising 90 per cent. of the alcohol in the mash, and quite free from fusel oil and acetaldehyde or foreshots.

2. **Fusel Oil** (tail-products), principally amyl alcohol, which forms an excellent oil for illuminating purposes and for the manufacture of fruit essences.

3. **Foreshots**, or **fore-runnings** (head-products), consisting of 97 per cent. acetaldehyde, and containing only 3 per cent. of alcohol. It forms an excellent material for denaturing purposes.

4. The alcohol-free **spent wash**, used as a food for cattle.

The types used in France and Germany differ to a considerable extent. A plant of each type will be described.

One of the best of the German stills is that of *Robert Ilges*, Germany, manufactured by the firm Gebrüder Sachsenberg, of Rosslau a/Elbe (Fig. 138).

The apparatus comprises essentially a distilling apparatus, consisting of a still A and a rectifier C, surmounted by a dephlegmator *l*, which together form a plant yielding alcohol vapours of about 96.5 per cent. free from fusel oil, but containing head-products. These vapours pass by a pipe *b* to a column D, where the head-products are completely separated.

The still A is of the "full" type devised by Ilges, and described on p. 302. It is fed with wash

in regulated quantity by means of a balance G, on which a funnel 2 is arranged to discharge into the feed pipe 3 of the still. The spent wash is discharged through a regulator R. A regulator P controls the supply of steam to the base *d* of the still.

The vapours evolved in the distilling column A, bearing with them all the easily and difficultly volatile impurities, such as aldehyde and fusel oil, pass through the tube *a* into the first *rectifying column* C, wherein the alcoholic vapours are strengthened to 96½ per cent., and the fusel oil liquefied and separated.

The rectifier C is of the film type devised by Ilges, and is packed with porcelain balls over which the liquid flows in intimate contact with the vapours. The dephlegmator *f* consists of horizontal cooling tubes with a packing of porcelain balls to produce an accompanying rectification.

A plate 8 at the base of the column is so constructed as to allow of the upward passage of vapours only. The liquid collecting on this plate consists of a dilute solution of alcohol containing tail-products, and is led away by a pipe 11 into the *cooler* J, where it is cooled to 30° C. This cooling causes the oil to separate completely from the water, and the mixture of oil and water runs into the *oil separator* M. The oil is lighter than the water and floats on its surface. The light oil, therefore, rises in the tube 13, and flows away by a pipe branching out at the point 15, while the water, now freed from oil, but containing alcohol, flows through a pipe 14 into a fusel oil distilling column R, and is distilled free from alcohol by a stream of steam entering at *d*. The alcoholic vapours pass by a pipe 7 to the base of the rectifier C.

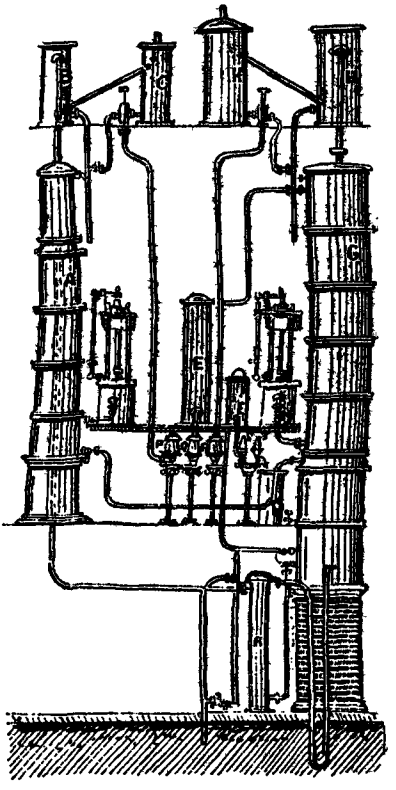


FIG. 137.—Barbet's Continuous Rectifying Plant.

After the alcoholic vapours have thus been completely deprived of their fusel oil in the rectifying column C, they enter the second *rectifying column* or purifier D, with a strength of 96.5 per cent. of alcohol by volume, but still containing the volatile **aldehyde and ethers**. It is the function of D to separate the pure alcohol from the aldehyde.

The column D is furnished with dephlegmators *p*, *q*, and tubular heaters *r*, S, through which steam circulates, and may conveniently be regarded as divided into three sections. The alcohol vapours of high degree entering the middle section by the pipe *b* are heated by passage through the heater *r* to a temperature sufficient to ensure a satisfactory removal of head-products from the liquid, about 70 per cent. of the vapours entering at *b* retrograding from the dephlegmator *p*. The uncondensed vapours from the dephlegmator *p* (about 30 per cent. of the total) enter the uppermost section and meet liquid (about 20 per cent. of the total) condensed in the dephlegmator *q*. The head-products are thus concentrated in the vapours (constituting 10 per cent. of the vapours entering at *b*) which survive the dephlegmator *q*, and are led by a pipe *c* to a refrigerator L. The liquid from the base of the middle section enters the lowermost section, and is partially vaporised by the heater *s*, to provide an up-flowing current of vapour which removes the last traces of head-products from the down-flowing alcohol. The purified liquid alcohol flows away by a pipe *h* to a refrigerator K.

In the German still just described, the alcohol is first concentrated and is then treated for the removal of head-products. In the French still about to be described, it should be noted as a salient feature of difference that the removal of head-products comes immediately after the distillation of the wash, and before the vapours are subjected to rectification. This still was devised by Guillaume and is manufactured by Egrot (Paris). The plant is shown diagrammatically in Fig. 140, and in its actual form in Fig. 139.

The wash is distilled in an inclined column A (Fig. 139) (not shown in Fig. 140) and the vapours enter a heat-exchanger *w* in the base of the rectifying column C, and are there condensed. The resulting phlegms flow through a pipe 3 (Fig. 140) to the purifying column B, where the head-products are volatilised and removed. By an ingenious artifice, to be subsequently described, the tail-products are made to behave as head-products, and are also removed. The purified phlegms pass through a pipe 4 to an accumulator or reservoir V, which is used by the inventor to produce a steadying or

fly-wheel effect on the plant. The phlegms overflow through a pipe 6 to an exhausting column E, which is entirely separate from the column B, and is so shown in Fig. 139, and the vapours there generated are led by a pipe *m* to a concentrating column G. The concentrated alcohol in the liquid form is led by a pipe 12 to the rectifying column C, and is there vaporised by the heat-exchanger *w*. The retrogradation in the column G is a weak spirit containing oils, and is led by a pipe 10 to the purifying-column B.

In the rectifying-column C, the last traces of tail-products are removed in the form of an alcoholic solution, and are led back to the column B by a pipe 25. The liquid alcohol, now almost pure, is led away by a pipe 16 to a final purifying column D, and is there subjected to a partial distillation for the removal of the last traces of head-products. The vapours pass by a pipe 37 to the rectifying column C, and the finished alcohol is led by a pipe 26 to the refrigerator. The condensers at the head of the columns B, C are arranged as described in the article on

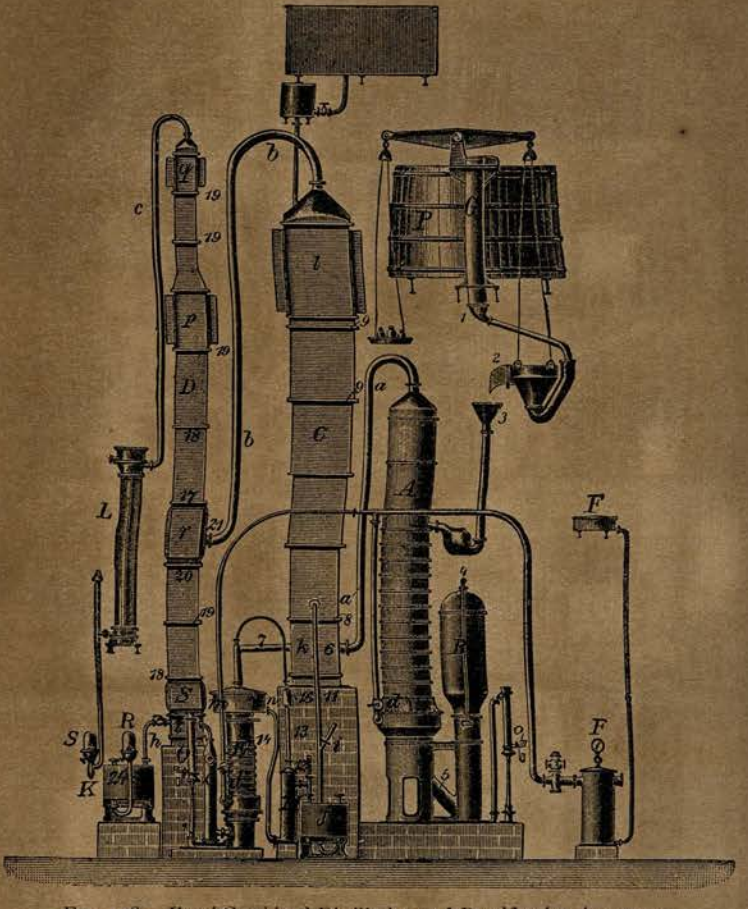


FIG. 138.—Ilges' Combined Distillation and Rectification Apparatus.

Regulation, p. 305, and provide distillates of head-products and an alcoholic solution of head-products respectively, the former being led to the refrigerator by a pipe 32, and the latter to the purifying column B by way of a pipe 24.

To return to the removal of the oils in the column B. It was shown in the article on Barbet's rectifying apparatus on p. 306, that fusel oils in the presence of water were more volatile than a dilute solution of alcohol. Guillaume (*vide* British Patent, No. 5,794, 1902), working on this basis, formed the idea of forcing the oils to behave as head-products by keeping the alcohol to the requisite low degree of dilution. In the purifying column, therefore, he provided a pipe 29 admitting water in sufficient quantity to ensure the volatilisation by the uprising vapours of the fusel oils contained in the down-flowing diluted alcohol. Above the point where the pipe 29 enters, the ordinary classification of products takes place, the aldehydes passing upwards as vapour, and the oils retrograding as liquid, and flowing away by a pipe 31 to the refrigerator.

It need scarcely be remarked that this article is far from being exhaustive. An attempt, however, has been made to describe the most important of the principles which have been adopted in the distillation and rectification of alcohol.

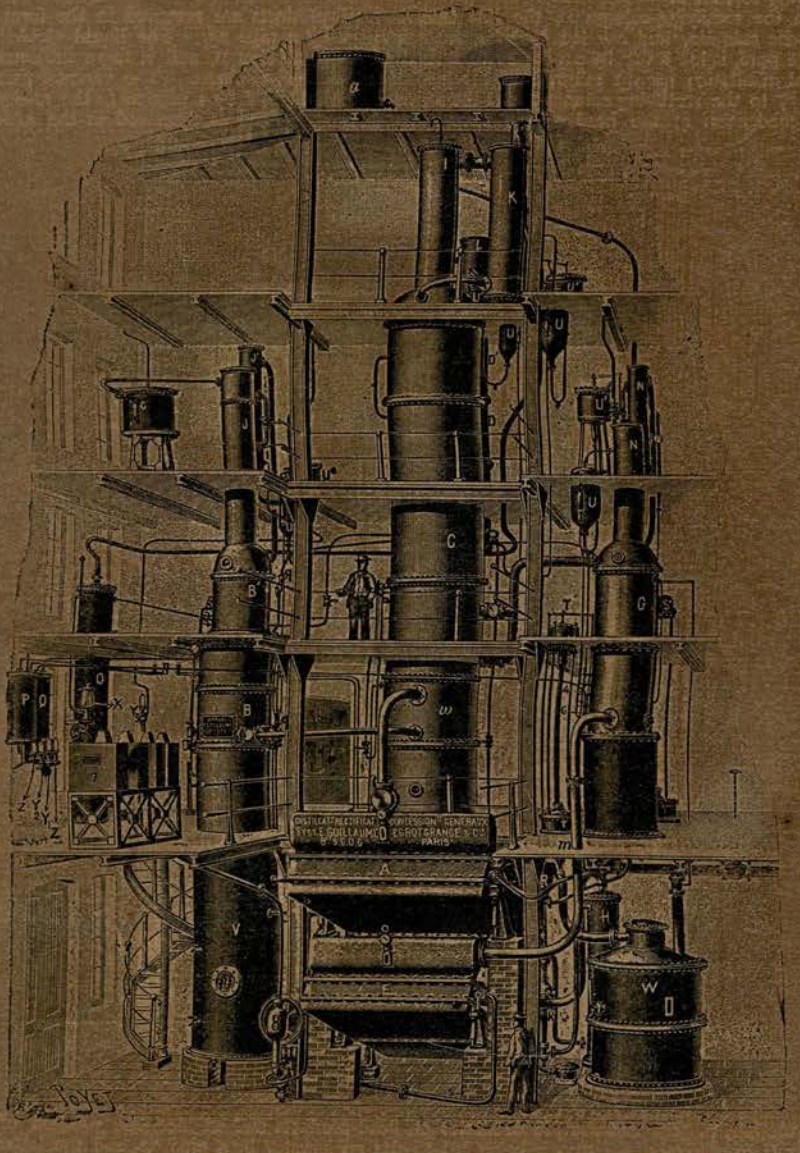


FIG. 139.—Guillaume's Continuous Distillation and Rectification Apparatus.

The plants described accordingly have been those which are most conveniently adapted for a discussion of these principles. It is only fair to say that numerous stills, other than those mentioned—for example, F. Pampe's low-pressure apparatus—are highly efficient and satisfactory in operation.

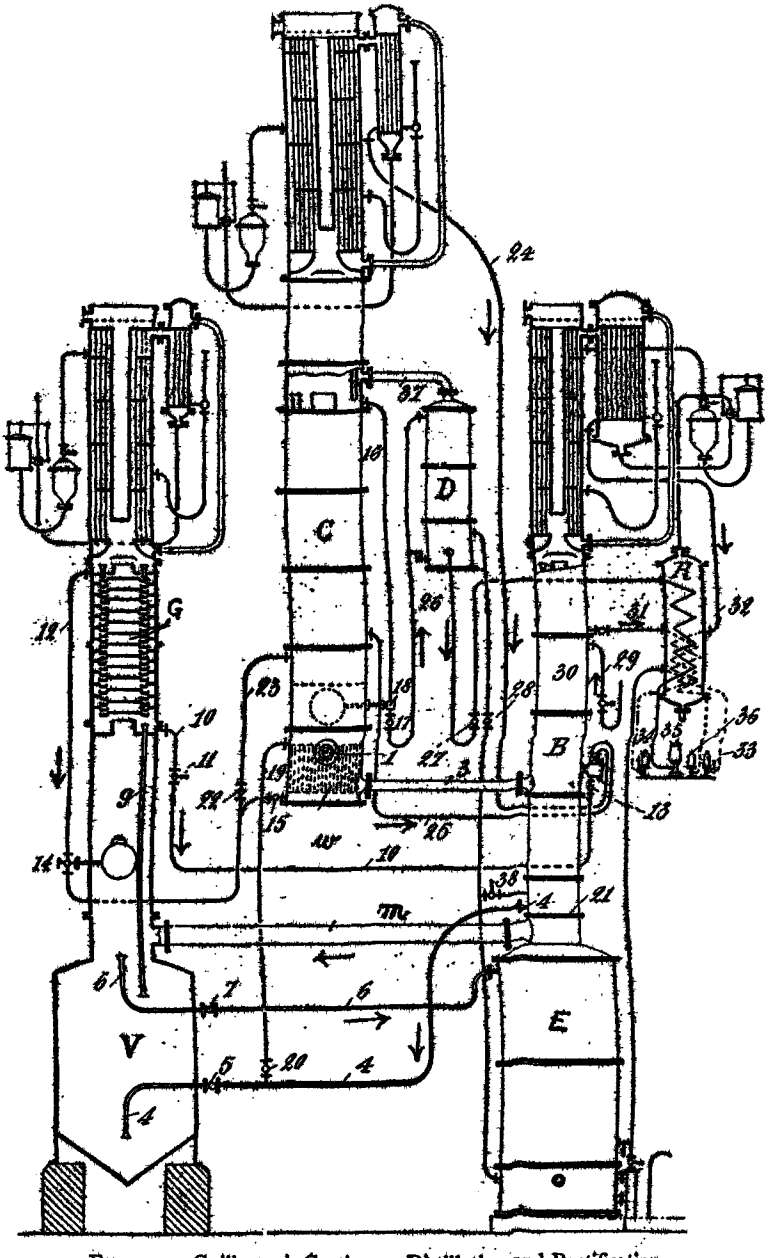


FIG. 140.—Guillaume's Continuous Distillation and Rectification Apparatus: Diagrammatic View.

STORAGE OF ALCOHOL

The alcohol is stored in large iron tanks, provided with inlet and outlet valves, and similar in construction to petroleum tanks. It is transported, like petroleum, in closed cistern trucks, which are filled and emptied by hose.

Utilisation of Spent Wash

The Spent Wash of corn and potato distilleries resulting after all the alcohol has been distilled off, contains a considerable amount of nitrogen and is used as a food for dairy cattle, beeves, and pigs. The spent wash from potato distilleries is usually made more nutritious by the addition of maize. In Germany the production of these cattle foods has already reached a very high stage of perfection, owing to the numerous "farmer distilleries" which thrive in country districts, such distilleries maintaining their own cattle. These spent washes must be fed warm to the cattle, fresh from the distillation, otherwise they rapidly sour and go bad. Fresh spent wash contains: 1.5-2 per cent. protein, 0.2-1 per cent. fats, 3-5 per cent. carbohydrate, and 90-94 per cent. water.

In large industrial distilleries in towns, where it is impossible to feed the wash to cattle in a fresh condition, the fluid is evaporated and sold as "dry wash." It then contains about 23 per cent. of protein, 35 per cent. of non-nitrogenous extractive substances, 11 per cent. fibres, and 6 per cent. of fat. This **dry wash** is transportable, but not so digestive as the fresh wash.

It has been proposed to place the purified spent yeast on the market as human food (see p. 275).

Alcoholometry—Testing the Spirit

Rectified Spirit of Wine, the most concentrated alcohol producible by ordinary distillation, contains 84 per cent. alcohol, sp. gr. 0.838.

Proof Spirit contains 49.24 per cent. alcohol, and has sp. gr. 0.91984 at 60°/60° F. Spirits weaker than this are said by the English Excise to be so many degrees (*i.e.*, so much per cent.) "under proof" (U.P.). Thus a spirit of 20° "under proof" means a liquid containing at 60° F. some 20 volumes of water and 80 volumes of proof spirit. A spirit of 50° U.P. contains 50 volumes water and 50 volumes "proof spirit." Pure water is 100° U.P.

"Over Proof" (O.P) Spirits are **stronger** than "proof spirit," and are defined by the number of volumes of proof spirit 100 volumes could yield when diluted with water. Thus 100 volumes of a spirit "50° O.P." on dilution with water would yield 150 volumes of "proof spirit." Absolute alcohol is 75.25° O.P. and hence 100 volumes when diluted with water can give 175.25 volumes of proof spirit. In the **United States** "proof spirit" has a sp. gr. 0.9341 at 60°/60° F. and contains 42.7 per cent. by weight of absolute alcohol.

The amount of alcohol in spirit is determined by taking its specific gravity with a hydrometer—here called an "alcoholometer." Pure alcohol at 15.5° C. (60° F.) has a specific gravity of 0.7946. The more water in the liquid, the more nearly the specific gravity approaches unity. The concentration of the alcohol is expressed by volume and by weight. Volume and weight percentages do not correspond, because in mixing water and alcohol a contraction ensues. (50 volumes alcohol + 50 volumes water yield only 96.4 volumes of diluted alcohol.)

The Volume Percentage, after Tralles and Brix, gives the number of cubic centimetres absolute alcohol contained in 100 c.c. of the fluid at 15.5° C. (60° F.).

The Weight Percentage (adopted officially since 1888 in Germany) gives the number of grams of absolute alcohol contained in 100 g. of the spirit at 15° C.

The "apparent" alcohol percentage, as read off on the graduations on the hydrometer immersed in the spirit at any given temperature, is reduced to the "True" alcohol percentage at the standard temperature, 15° C. in Germany, and 60° F. in England, by means of special tables.

The spirit is sold on the basis of the amount of absolute alcohol (100 per cent.) it contains. The percentage of alcohol by volume and weight contained in watery solutions of various specific gravities is expressed by the following table:—

SPECIFIC GRAVITY OF PERCENTAGE MIXTURES OF ALCOHOL AND WATER BY VOLUME AND BY WEIGHT AT 60° F. ($15\frac{5}{9}$° C.)

Per Cent. Alcohol.	Per Cent. by Volume.	Per Cent. by Weight.	Per Cent. Alcohol.	Per Cent. by Volume.	Per Cent. by Weight.	Per Cent. Alcohol.	Per Cent. by Volume.	Per Cent. by Weight.
	Corresponding Specific Gravity.			Corresponding Specific Gravity.			Corresponding Specific Gravity.	
1	0.9985	0.9981	35	0.9592	0.9490	69	0.8925	0.8748
2	.9970	.9963	36	.9579	.9472	70	.8900	.8724
3	.9956	.9944	37	.9565	.9453	71	.8875	.8700
4	.9942	.9928	38	.9550	.9433	72	.8850	.8676
5	.9928	.9912	39	.9535	.9413	73	.8825	.8652
6	.9915	.9896	40	.9519	.9394	74	.8799	.8629
7	.9902	.9880	41	.9503	.9374	75	.8773	.8605
8	.9890	.9866	42	.9487	.9353	76	.8747	.8581
9	.9878	.9852	43	.9470	.9332	77	.8720	.8557
10	.9866	.9839	44	.9452	.9311	78	.8693	.8533
11	.9854	.9826	45	.9435	.9291	79	.8666	.8509
12	.9843	.9813	46	.9417	.9269	80	.8639	.8484
13	.9832	.9800	47	.9399	.9248	81	.8611	.8459
14	.9821	.9788	48	.9381	.9227	82	.8583	.8435
15	.9811	.9775	49	.9362	.9204	83	.8555	.8409
16	.9800	.9763	50	.9343	.9183	84	.8526	.8385
17	.9790	.9751	51	.9323	.9160	85	.8496	.8359
18	.9780	.9739	52	.9303	.9138	86	.8466	.8333
19	.9770	.9727	53	.9283	.9116	87	.8436	.8307
20	.9760	.9714	54	.9263	.9094	88	.8405	.8282
21	.9750	.9702	55	.9242	.9072	89	.8373	.8256
22	.9740	.9690	56	.9221	.9049	90	.8339	.8229
23	.9729	.9677	57	.9200	.9027	91	.8306	.8203
24	.9719	.9664	58	.9178	.9004	92	.8272	.8176
25	.9709	.9651	59	.9156	.8981	93	.8237	.8149
26	.9698	.9637	60	.9134	.8958	94	.8201	.8122
27	.9688	.9622	61	.9112	.8935	95	.8164	.8094
28	.9677	.9607	62	.9090	.8911	96	.8125	.8065
29	.9666	.9592	63	.9067	.8888	97	.8084	.8036
30	.9655	.9577	64	.9044	.8865	98	.8041	.8006
31	.9643	.9560	65	.9021	.8842	99	.7995	.7976
32	.9631	.9544	66	.8997	.8818	100	.7946	.7946
33	.9618	.9526	67	.8973	.8795			
34	.9605	.9508	68	.8949	.8772			

The spirit is also usually subjected to the following tests (for fuller details, see Allen's "Commercial Analysis," 1909, vol. i.):—

1. **Amount of Fusel Oil** (Higher alcohols).—In England and America this is usually estimated by the *Allen-Marquart* method, which consists in boiling the sample with KOH, steam distilling, adding saturated brine to distillate to separate fusel oil, and extracting with CCl_4, oxidising with $K_2Cr_2O_7 + H_2SO_4$, titrating with $\frac{N}{10}$ $Ba(OH)_2$, using methyl orange as indicator at first, and then phenolphthalein. Each c.c. of $\frac{N}{10}$ alkali required in the second stage of the titration (using phenolphthalein) corresponds to 0.0088 g. amyl alcohol. The official German method (Röse-Herzfeld) is to shake the spirit with chloroform under rigorously defined conditions. The increase of volume gives the amount of fusel oil.

2. **Aldehyde Determination.**—This is estimated colorimetrically by means of Schiff's reagent.

3. The **Furfurol** is estimated by comparing the tint produced in the liquid by the addition of aniline acetate with that produced in a standard solution of furfurol in pure 50 per cent. alcohol. A first-class prima spirit should contain 94 per cent. alcohol by weight (96 by volume), possess a neutral taste and smell, be of a white colour, be quite neutral, contain no aldehyde or furfurol; should remain clear and colourless when mixed with water; with $KMnO_4$ solution should remain red after thirty minutes; boiled with H_2SO_4 (Savalle's test) should give no colour; treated with H_2SO_4 in the cold (Vitali's test) should give no colour.

Acknowledgment.—The authors have much pleasure in thanking the firm of John Dewar & Sons Ltd., distillers, of Perth, for much help and scientific information regarding alcohol manufacture, which, in their hands, has already reached a very high state of perfection.

Fusel Oils and the Manufacture of Amyl and Butyl Alcohol

Whisky, brandies, and similar alcoholic fluids sometimes contain as much as 0.6 per cent. of fusel oils, which contain esters, and are of value in giving a characteristic odour to the liquid. Potato spirit fusel oils have an unpleasant taste and smell.

It is the *quality*, not so much as the *quantity*, of the fusel oil present in a spirit which affects its taste, and decides whether it must be refined or not. Many valuers rely on taste alone for the determination of this important point.

Fusel oil was until recently an almost valueless by-product of the spirit industry, but is now a very valuable substance.

Manufacture.—The manufacture by the distillation of wine and especially spirits has been described above (pp. 251, 298, 300, 307, 308, 309). By the processes above described it was necessary to manufacture 1,000 parts of ethyl alcohol for every one of fusel oil produced. *Prof. Fernbach* of the Pasteur Institute has worked out a process whereby starch is directly fermented to fusel oil and acetone. Mashes are made of cereal grains (*e.g.*, maize) or potatoes, and inoculated with special cultures, whereby over 42 per cent. of the starch employed is converted into mixed higher alcohols (fusel oils) and, Fernbach states, of these about 65 per cent. is butyl alcohol. O. Hehner found that 100 parts of the dried substance of potatoes yielded 43 parts of higher alcohols plus acetone, the latter constituting above one-third. It is asserted that these fusel oils can be placed on the market at a price not exceeding £35-£45 per ton (see W. H. Perkin, jun., *Journ. Soc. Chem. Ind.*, 1912, p. 622; also English Patents, 15,203, 1911; 15,204, 1911; 21,073 1912).

Composition of Fusel Oils.—The composition of **Wine Fusel Oils** is given on p. 251. They consist, roughly, of 51 per cent. *normal butyl alcohol*, 20 per cent. *amyl alcohol*, 10 per cent. *normal propyl alcohol*, 8 per cent. *ethyl acetate*, 8 per cent. *acetal*, and small amounts of *esters of fatty acids, acetaldehyde, heptyl alcohol, amine bases*, etc.

The composition of **Spirit Fusel Oils** varies considerably with the method of manufacture, but consists mainly of amyl alcohol. W. E. Bell gives the following analysis of a sample of the fusel oils removed from the "**hot feints**" receiver of a Coffey Still (p. 298):—

Amyl alcohol (B.P. 132° C.), 42.2 per cent.; *isobutyl alcohol* (B.P. 109° C.), 33.4 per cent.; *normal propyl alcohol* (B.P. 97° C.), 18.9 per cent.; *ethyl alcohol*, 3.5 per cent. Ethyl esters of palmitic and oleic acid were also present.

A sample of **Commercial Fusel Oil** contained: *Amyl alcohol* (B.P. 132° C.), 68 per cent.; *isobutyl alcohol* (B.P. 109° C.), 24 per cent.; *normal propyl alcohol* (B.P. 97°), 7 per cent.; small quantities of *esters, furfural*, etc.

When commercial fusel oil is fractionated the portions boiling at 128°-131° C. consist of the **Amyl Alcohols**, containing 87 per cent. **isoamyl alcohol**, $(CH_3)_2CH.CH_2.CH_2OH$, and 13 per cent. **active amyl alcohol**, $CH_3.CH_2CH(CH_3).CH_2OH$.

The fusel oil produced by **Fernbach's Fermentation Process** contains about 65 per cent. of **butyl alcohol**.

Uses of Fusel Oils and Higher Alcohols.—Fusel oil was, until recently, used as an illuminating oil, but is now far too expensive for this purpose. It is very largely used for manufacturing the individual higher alcohols (by fractional distillation) and their esters, thus giving rise to the industry of **Fruit Essences** (see p. 382) for flavouring liquors, jellies, sweets, etc. Very large quantities of **amyl acetate** are used as a solvent for pyroxyline (nitrocellulose) for the purpose of making nitrocellulose varnishes, lacquers, and for artificial leathers having a nitrocellulose composition (see pp. 49, 383, 589). It was formerly employed as a solvent in the explosive and paint industry, but its high price has caused an abandonment of it in favour of cheaper solvents. Amyl alcohol is used in the flotation process of separating sulphide ores, its usefulness depending upon the low surface tension of its aqueous solution. Fusel oil and its constituent alcohols have been employed for the precipitation of asphalt from heavy mineral oils. Recently the *Synthetic Products Company* of London have proposed to place it on the market by *Fernbach's Fermentation Process*, and to utilise the product for the manufacture of **synthetic rubber** by methods worked out by Perkins, Matthews, and others (see W. H. Perkins, *Journ. Soc. Chem. Ind.*, 1912, pp. 620-623). Butyl alcohol is stated to be an excellent "Burn" cure.

Statistics.—In Germany in 1900-1901 the oil sold at 50 M. for 100 kilos, or 4½ lbs. a shilling. By 1910 its price had risen to 170 M. per 100 kilos. In 1912 it was quoted at £140 a ton. The world's supply in 1912 was variously estimated at 3,500 to 6,000 tons annually, and until recently it was necessary to manufacture 1,000 parts of alcohol for every one of fusel oil. By *Fernbach's Fermentation Process* it is stated that it can be produced in unlimited amount at £35-£40 a ton. The *United States* in 1910 imported 4,954,000 lbs. (value, $598,000) of fusel oil, Russia supplying one-third of the quantity. No less than 450,000 gals. of amyl acetate are annually consumed in the United States for solvent purposes (nitrocellulose varnishes).

VI.—VINEGAR, LACTIC ACID, BUTYRIC ACID

By G. Martin, Ph.D., M.Sc.

VINEGAR

LITERATURE

C. Ainsworth Mitchell.—"The Vinegar Industry." *Knowledge*, June 1911, p. 219.
W. T. Brannt.—"Manufacture of Vinegar and Acetates." London, 1901.
J. Bersch.—"Essig-fabrikation." Vienna, 1901.
P. Hassach.—"Gärungs-essig." Vienna, 1904.
Rothenbach.—"Organismen des Gärungsessigs." 1907.

For **Acetic Acid** see under **Destructive Distillation of Wood**. For **Acetic Acid Bacteria** see under **Bacteria**, p. 224.

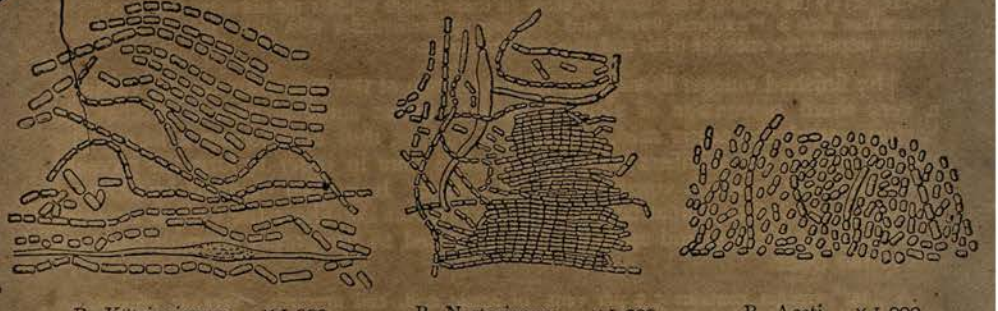
Vinegar consists of a weak solution (4-10 per cent.) of acetic acid in aqueous liquors prepared by the oxidation of alcoholic liquors by means of acetic acid bacteria, *Bacterium aceti*, many varieties of which exist, the best races being propagated by pure culture methods (see p. 231) and used for impregnating the alcoholic liquors to be fermented.

The *Bacterium aceti* will not grow in a pure aqueous solution of alcohol; they require, besides alcohol, the presence of nitrogenous matter and salts to serve as food. Consequently the starting-point in the manufacture of vinegar consists of an alcoholic liquor such as wine, beer, and alcoholic mashes generally.

The bulk of English made vinegar is manufactured from **malt**, or a mixture of malt with grain and sugar. The malt or malt and grain is crushed, and heated in a mash-tun with water at a gradually increasing temperature until the starch is converted into sugar by the diastase in the malt, as described under **Brewing**, the resulting liquid being known as **wort**.

Often the wort is obtained by the **conversion process**. The grain, usually rice or maize and free from malt, is treated with dilute H_2SO_4 in a closed vessel termed a **converter**. The acid hydrolyses the starch to produce a saccharine solution which is then freed from acid by calcium carbonate, and the liquor separated from the precipitated calcium sulphate.

The wort is now pitched with yeast and is aerated and kept at the right temperature so as to convert as much as possible of the sugar into alcohol. The subsequent strength of the vinegar depends largely upon the success of this stage, because all saccharine matter (also dextrines) escaping the action of the yeast also



B. Kützingianum. × 1,000. B. Nastorianum. × 1,000. B. Aceti. × 1,000.

Fig. 141.—Acetic Acid Bacteria (Hansen).

remain unattacked by the acetic bacteria. The resulting liquor, called **gyle**, and containing 6-7 per cent. of alcohol, is treated with the acetic acid bacteria, the alcohol being oxidised to acetic acid, thus:—

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O.$$

Many other compounds are simultaneously formed, especially aldehyde, which is produced as an intermediate stage in the oxidation:—

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Oxygen.}}{O} = \underset{\text{Aldehyde.}}{C_2H_4O} + H_2O.$$

The acetifiers employed consist of a large wooden vat provided with a perforated false bottom and numerous holes in the sides for the admission of air. The interior of the vat is filled with basket-work (formerly beech shavings), and a rotating sparger is used for sprinkling the gyle uniformly over the material.

Fig. 142 shows a section of the upper portion of an acetifier. The gyle, impregnated with acetic acid bacteria, is pumped from the bottom of the vat and discharged into the funnel at the top, which is boxed in to prevent loss by evaporation. The liquid flows down the tube G, enters the sparger R, which revolves on the pivot S. In the arms of the sparger are a number of small holes through which the liquid rushes, thus causing the sparger to revolve steadily and uniformly sprinkle the surface of the basket-work. The acetic bacteria multiply on the surfaces of the basket-work, generating heat and rapidly oxidising the alcohol as it passes over them. A thermometer inserted through a hole in the side of the acetifier indicates the temperature within.

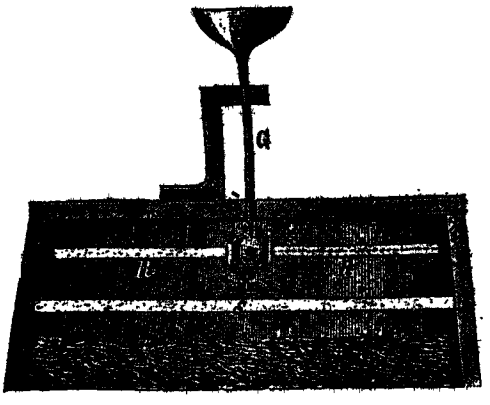


FIG. 142.—Section of the Upper Part of Modern Acetifier.
(After C. A. Mitchell. See *Knowledge*, June 1911.)

According to Mitchell (see above) the species of acetic bacteria most used in England are most active at 105° F. (40.6° C.) and flourish well at 110° F. (43.3° C.). The bacteria used on the Continent are seldom worked above 95° F.

For successful working the conditions are: (1) a regular and uniform supply of air to the bacteria; (2) maintenance of the correct temperature in the acetifier. In the presence of too much air the bacteria oxidise part of the acetic acid to CO_2, and the resulting vinegar is weak. On the other hand if too little air is supplied the bacteria unite together into a slimy mass (mother-of-vinegar) by the swelling and fusion together of their outside cellular membranes, thus converting themselves into a "zoogloeal form" and clogging up the acetifier with slimy masses which still further impede the entrance of air and stop uniform aeration.

The finished vinegar flowing out at the bottom of the apparatus usually contains a very small percentage of alcohol, because unless some alcohol is present the bacteria attack the acetic acid, oxidising it further, thus occasioning a loss. The vinegar leaving the acetifiers is stored for some time in order to form the pleasant-smelling esters to which vinegar owes its aroma. It is then clarified by filtration through fine sand or similar substance. As it leaves the filters the vinegar contains 6 per cent. acetic acid and upwards. It is diluted to the proper strength and sent out to the trade.

A "24" vinegar contains 5.5 per cent. of acetic acid, and upwards. Weaker vinegars are known as "22," "20," "18," and "16," the latter of these containing 4.1 per cent. of acid. The numbers originally referred to the number of grains of sodium carbonate required to neutralise the acid in one fluid ounce of the vinegar.

A very cheap vinegar containing 3.5 per cent. of vinegar is sometimes sold under the name "Diamond." Usually, however, vinegars contain more than 4 per cent. of acetic acid. The yield of acetic acid is usually about 70-80 per cent. of theory, the loss of acidity due to evaporation of the alcohol and destruction of acetic acid (due to irregular aeration) ranging from 10-20 per cent., and sometimes, in faulty apparatus, even to 30 per cent.

Cheap vinegars are sometimes "faked" by diluting distilled acetic acid (obtained from wood) with water to the proper degree, and colouring it with caramel or burnt sugar. Some vinegars are aromatised with fennel, caraway, and similar substances, others are coloured red, and some are even adulterated with dilute H_2SO_4.

Wine Vinegar is not manufactured in England on account of the absence of wine. On the Continent, however, it is an important industry. The wine (usually a sour kind of poor quality) is treated with acetic acid bacteria, and in the quick process is allowed to flow through vats containing beech shavings or basket-work as above described. The best **wine vinegars**, however, are made by the **Orleans Process**. Oaken vats, of 2-4 hl. capacity, and provided with air-holes in their upper parts, are placed in chambers kept at 20°-25° C., and one-fifth filled with a hot strong wine vinegar; this partially soaks into the wood and deprives it of its woody taste. Next 10 l. of wine are added, and the liquid allowed to stand, usually after impregnating it with a small amount of a pure culture of acetic acid bacteria. The bacteria develop rapidly, covering the liquid with a film of slimy "mother-of-vinegar." The alcohol is oxidised to acetic acid, which sinks to the lower part of the liquid, the light alcohol accumulating gradually at the surface. After about a week another 10 l. of wine are added, and the process repeated until the vat is half full. Then a third of the finished vinegar is withdrawn, and the addition of wine continued as before. Wine vinegar is much valued for its pleasant bouquet.

Vinegar is used for flavouring meat, etc., and also for making white lead (which see).

Statistics.—The English imports of **Vinegar** and **Acetic Acid** for table use: 1906, 258,089 gals.; 1908, 459,502 gals.; 1910, 212,696 gals.; value in 1910=£13,400. The export was: 1906, 569,182 gals.; 1908, 768,742 gals.; 1910, 880,017 gals.; value in 1910=£105,800. The U.S.A. in 1910 imported 310,000 gals. (value $79,000), and exported 115,000 gals. (value $13,000).

Acknowledgment.—I have to thank Mr Ainsworth Mitchell, B.A., F.I.C., for calling my attention to errors in the current descriptions of the vinegar process, published in the older text-books. My best thanks are due to the editor of *Knowledge* for lending blocks.

LACTIC ACID, $CH_3CH(OH).COOH$

LITERATURE

A. A. CLAFLIN.—"The Manufacture and Applications of Lactic Acid." *Journ. Chem. Ind.*, 1897, 16, 516.

C. WEHMER.—"Über Lebensdauer und Leistungsfähigkeit technischer Milchsäurebakterien." *Ch. Zeit.*, 1906, 30, 1033.

G. SCHÄFER.—"Die Fortschritte auf dem Gebiete der Milchsäurefabrikation." *Ch. Zeitschr.*, 1907, 6, 117 and 189.

H. EMDE.—"Milchsäure." Dammer's "Chemische Technologie der Neuzeit," i. 674, 1910.

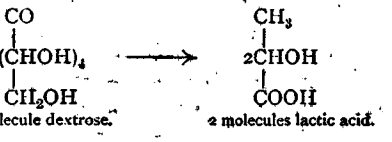
DOUGLAS.—"The Bacillus of a Long Life." London, 1911.

G. HERSCHEL.—"Soured Milk." London, 1909.

Ethylidene lactic acid is now prepared on a large scale in America, Great Britain, and Europe. It is a rapidly growing industry—a result due to the recent introduction of pure cultures of the lactic acid bacillus into the industry. In England the industry has been in existence for nearly thirty years, being originated by Mr Avery by processes patented between 1881-1884.

In Germany up to 1895 no factory existed for the supply of lactic acid, all the lactic acid being imported from England. At the present time thirty factories have since come into existence, the largest being the Firm C. H. Böhringer u. Sohn in N. Ingelheim. This latter firm alone produces 500,000 kg. of technical lactic acid. In the *United States* the industry is an old and well-established one; thus so long ago as 1895 the *United States* consumed 1,000,000 lbs. and exported 500,000 lbs. In 1896 the domestic consumption was 1,200,000, and the foreign 1,000,000 lbs.

The manufacture is carried out by allowing the micro-organism known as *Bacillus acidi lactici* (of which there exist many races) to split up by fermentation a solution containing grape sugar, when the following change takes place:—



Avery's Process

Preparation of the Saccharine Solution.—The solution should have a sp. gr. of 1.05-1.075, and contain 7½-11 per cent. of glucose. It is advantageous to replace 10-15 per cent. of the glucose by cane sugar, which is progressively inverted by the lactic acid, and this continually furnishes fresh matter for the bacillus. The solution should contain nitrogenous food (not under 2 parts nitrogen to 100 parts sugar in vat) for the bacillus. An extract of vegetable albumen, made by extracting bran with boiling water and dilute acid, is very suitable; or mineral nitrates and ammonium salts may be used.

Process of Impregnation.—The saccharine solution made up as described above is boiled for one hour to sterilise it, rapidly cooled between 55° C. and 45° C., run into the fermentation vat, and impregnated with the *Bacillus acidi lactici*. In continuous manufacture the impregnation is carried out by running in 20 per cent. or more of a preceding fermenting liquor, in which a lively fermentation is in progress. But for the original impregnation a good culture of the lactic bacteria must be obtained by allowing milk to stand at 45° C. until slightly sour. A pure culture is usually obtained by impregnating previously sterilised milk, kept at 45° C., with a good lactic acid bacteria obtained from the bacteria in a ferment tank. The best variety of *Bacillus acidi lactici* is 2-2.5 μ long, and 1 μ in diameter.

Process of Fermentation.—During the process of fermentation the temperature of the saccharine liquid is kept between 45° and 55° C. in order to avoid the development in the liquid of **butyric acid** or **alcoholic** ferments. Since the *Bacillus acidi lactici* cannot flourish in solutions containing more than 1 per cent. of lactic acid, the acid as it is produced is continually removed by the addition of chalk dust suspended in water, in such proportion as to keep the lactic acid within the limits 0.02-0.5 per cent. If the neutralisation is carried too far, so as to lower the percentage of lactic acid below these limits, butyric acid fermentation may set in and spoil the yield. The fermentation should proceed vigorously and be completed in three to six days when 98 per cent. of sugar is used up. The liquor, which is a solution of calcium lactate, is then heated sharply to kill all bacteria and spores, filtered from the dead bodies of the bacteria, and evaporated. Pure lactic acid may be obtained by repeated crystallisation of the calcium lactate; but a commercial lactic acid is obtained merely by decomposition of the uncrystallised solution by sulphuric acid. The free acid is filtered from the $CaSO_4$ (which is practically insoluble in the dilute lactic acid) and evaporated to a 50 per cent. solution, when it forms a brownish syrupy liquid, of sp. gr. 1.20, containing about 7 per cent. lactic anhydride.

German Methods of Manufacture.—The solution of grape sugar is always made from a mash of starchy material (maize, potatoes, rice, etc.) by treating with malt in order to convert the starch into maltose, just as in the manufacture of spirits. The lactic acid bacillus employed in the largest German factories is the *Bacillus acidi lactici*, Hüppe, forming short thin rods (6 μ. and more long), linked together in chains; it is sporeless. A pure culture of this bacillus is obtained by the ordinary methods of bacteriology from sour milk or cheese, using as growing medium a solution of 100 parts grape sugar, 1 part dried peptone, 0.2 part potassium hydrogen phosphate, 1 part sal-ammoniac, 50 parts of powdered chalk, and 600 parts of water.

The fermentation is carried out, much as in Avery's process, at a temperature of 45°; but the time of fermentation is usually ten to twelve days. At the end of this time the absence of sugar is proved by Fehling's solution, the mass is then made weakly alkaline with lime water, boiled, filtered, and evaporated to 15° Bé., when the calcium lactate crystallises out and is filter-pressed away from the dark mother-liquors, which, united with the washings, are again evaporated to 15° Bé. and allowed to crystallise, the black mother-liquors running to waste.

The calcium lactate is purified by crystallising and decomposed by H_2SO_4, filter-pressed from the precipitated $CaSO_4$, and the solution of the acid concentrated by evaporation. If a clear lactic acid solution is required, the warm solution of lactic acid from the gypsum filter presses is pumped into tall wooden or leaden cylinders filled with animal charcoal, left there for some hours, drawn off at the bottom, filtered through felt cloth, and evaporated to 50 per cent. acid.

Chemically pure lactic acid is obtained by decomposing calcium lactate with zinc carbonate, whereby the sparingly soluble and easily crystallisable zinc lactate is obtained. The pure zinc lactate is then decomposed by H_2S, filtered from the ZnS—a difficult operation rendered easier by adding animal charcoal, paper pulp, etc.—and evaporated in an enamelled vacuum apparatus; when clear, pure lactic acid is obtained.

It is also obtained pure by distilling syrupy (26° Bé.) commercial lactic acid with superheated steam at 140°-160° C. from a calcium chloride bath. At 140° C. acetic acid, butyric acid, etc., distils, then comes pure lactic acid or anhydride. The concentrated distillate is decolourised by sunlight, animal charcoal, etc. 20-30 per cent. of the lactic acid is lost owing to the formation of lactic anhydride.

Another method is to shake the lactic acid for twenty-four hours with three times its volume of ether in a glass balloon. The impurities settle on the walls of the vessel. The clear ethereal solution is then forced by means of compressed air into another glass balloon, is there decolourised with animal charcoal, filtered through paper or cotton cloth, the ether distilled over and used again, and traces of the ether in the acid removed by blowing in warm air.

A proposed method (German Patent, 171,835) of purification is to convert the lactic acid into its ethyl ester (by boiling with ethyl alcohol and a little normal acid) and distilling *in vacuo*. The pure ester thus obtained is then decomposed by blowing through steam, the alcohol distilling over and the lactic acid remaining, being concentrated by evaporation.

The pure acid costs five to six times as much as the commercial variety.

Properties.—Pure anhydrous lactic acid, obtained by repeated rectification *in vacuo*, is a crystalline mass—M.P. 18° C.; B.P. 119°-120°.

Commercial *pure* 75 per cent. lactic acid is a syrupy, clear fluid, containing 8 per cent. lactic anhydride.

Salts.—The calcium and zinc salts occur in commerce, forming a convenient means for transport of lactic acid. The iron salt is used medicinally. Antimony lactate is used to an increasing extent as a substitute for tartar emetic in dyeing and printing calico. Certain double salts of antimony lactate with alkalies, alkaline earths, and zinc salts are largely manufactured for the purpose under such names as **Lactolin, Antimonin**. For preparation see German Patents, 98,939, 136,135, 148,069.

The **Titanium** salts (German Patents, 136,009, 149,577) are used in dyeing leather.

Uses.—See above, under **Salts.** Lactic acid, since its increased production and consequent fall in price, is used to a very large extent in dyeing wool as an assistant in mordanting with potassium bichromate. It is also largely used in tanning for removing the lime from the skin (J. T. Wood, *Journ. Chem. Ind.*, 1885, 27 *et seq.*; F. Andreasch, *Der Gerber*, 21, 506; 22, 513). It is used to a limited extent in spirit manufacture for souring the yeast in order to prevent the development of injurious fermentation.

Statistics. — *German Imports:* 1909, 30 dz.*; 1908, 20 dz. *Exports:* 1909, 10,470 dz.; 1908, 9,720 dz.

The English exports are very considerable, but owing to the haphazard way the materials exported are classified no information is obtainable from the Custom House returns.

BUTYRIC ACID

Normal butyric acid, $CH_3.(CH_2)_2COOH$, is usually obtained in a similar manner to lactic acid (above described) by fermentation of sugar or starch in the presence of calcium carbonate. Formerly the fermentation was effected by adding to the solution small amounts of decaying cheese, and keeping the solution at 25°-35° C. Now, however, the liquor is usually impregnated with pure cultures of butyric acid bacteria. According to Fitz ("Ber.," 11, 49, 53) cultures of *Bacillus subtilis* and *Bacillus boocapricus* are especially efficient. The calcium butyrate resulting from the fermentation is transformed into the sodium salts by treating with Na_2CO_3, and the butyric acid liberated by H_2SO_4. The butyric acid is separated by fractional distillation from acetic or caprionic acids, which are usually found present in small amount. By converting the acid into the ethyl ester, fractionating this, and again regenerating the acid by hydrolysis, the chemically pure acid may be obtained. Oily liquid, with an unpleasant, rancid smell—B.P. 162° C.; M.P. −7.9° C.; sp. gr. 0.978.

* 1 dz. = 100 kg. = about $\frac{1}{10}$ ton.

SECTION VI

The Charcoal and Wood-Distilling Industries

INCLUDING THE

Manufacture of Methyl Alcohol, Acetone, and Acetic Acid

THE CHARCOAL AND WOOD-DISTILLING INDUSTRIES

INCLUDING THE MANUFACTURE OF METHYL ALCOHOL, ACETONE, AND ACETIC ACID

By G. Martin, Ph.D., M.Sc.

LITERATURE

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The preparation of **wood charcoal** by burning wood in a supply of air insufficient for complete combustion is a very old industry which is still carried out to some extent in countries rich in wood—such as in the Harz, Steiermark, Sweden, Finland, Russia (Ural), etc., and the charcoal so obtained is much valued as a fuel, since it is free from sulphur and leaves little ash when burned. The charcoal is also used for making gunpowder, for purifying spirits, for packing in refrigerators, and for other purposes as well.

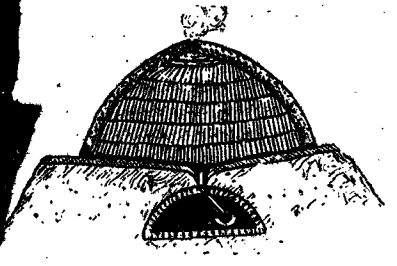

Fig. 143.—Charcoal Kiln, with Depression on Floor for Collecting Wood Tar.

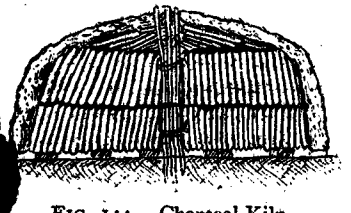

Fig. 144.—Charcoal Kiln, Ordinary Type.

The operation is carried out in "**Meilers**" or "**Kilns**": the wood is piled symmetrically round a central narrow shaft, and the wood is covered with a layer of charcoal, earth, and twigs. The wood is lighted in the *middle* at the bottom. A part of the wood burns, and the heat thus produced reduces the rest to charcoal. The charring proceeds from the centre outwards, and the volume of the wood diminishes. Holes are finally made in the external covering in order to conduct the combustion in any required direction so that all the wood may be completely charred. The

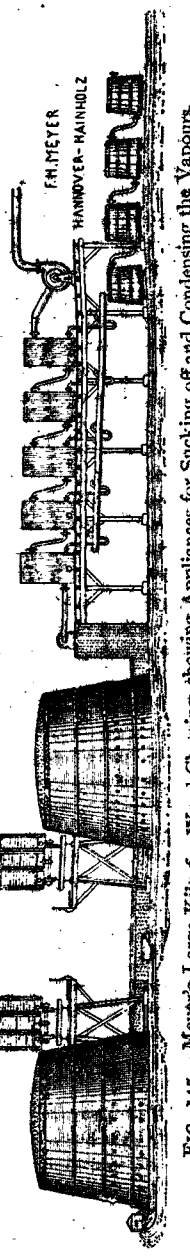

Fig. 145.—Meyer's Large Kiln for Wood Charring, showing Appliances for Sucking off and Condensing the Vapours.

air supply must be so regulated that an actual *flame* never appears. The burning may last a week or more. 100 cub. yd. of dry wood yield 50-75 cub. yd. of charcoal. 100 parts by weight of wood containing 25 per cent. water yield 20-28 parts of charcoal containing 89-90 per cent. C, 1-2 per cent. H, 2-4 per cent. O, 2-11 per cent. water, and 3 per cent. ash.

In Sweden, Russia, and U.S. America, a considerable amount of **wood tar** is obtained by burning in this manner, or in masonry kilns. Depressions are made in the floor of the kiln under-

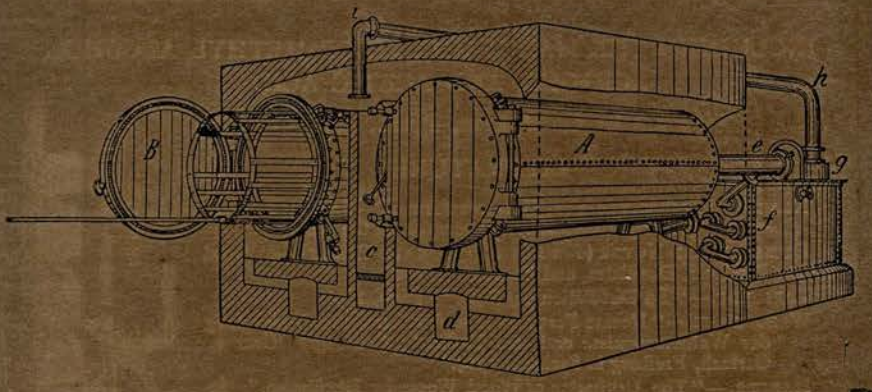

FIG. 146.—Small Retorts for Wood Distillation.
(F. H. Meyer, Hannover-Hainholz, Germany.)

neath the layer of wood (Fig. 143). The tar flowing from the heated wood into these passes by a channel into a vessel outside the kiln, and is there collected.

Freshly made charcoal is spontaneously combustible and very hygroscopic. Its calorific value about 7,000 calories. In this process all the valuable volatile products are completely lost.

F. H. Meyer (Hanover) has designed large kilns (Fig. 145) with appliances for sucking vapours, and thus gaining a large yield of volatile distillates. That shown in the illustration ta 300 cub. m. of wood with a working time of twenty days.

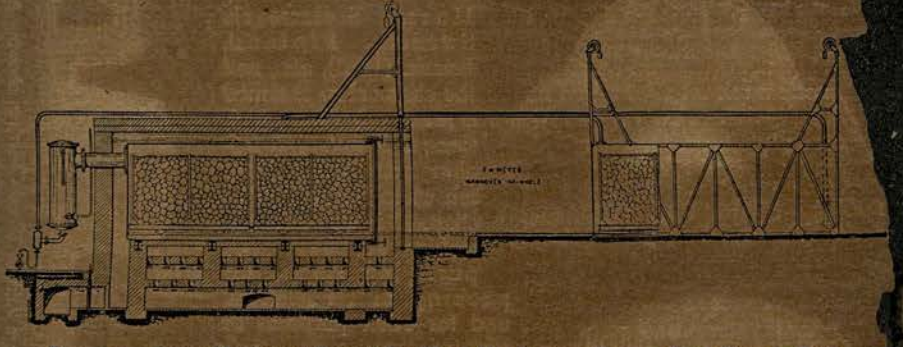

FIG. 147.—Large Horizontal Retorts for Wood Distillation, showing Wire Cage on Rails.
(F. H. Meyer, Hannover-Hainholz, Germany.)

Destructive Distillation of Wood from Closed Retorts

The advantage of this process is that it allows the recovery of all the volati products. The disadvantage is that the retorts are necessarily restricted in size, and consequently will not take in much wood at a time. The yield of charcoal and distillate depends very greatly both upon the nature of the wood and the manner in which the distillation is carried out. Thus if the heating be carried out rapidly in small retorts and at a high temperature, much gas and little charcoal is produced,

also little acetic acid and tar; while heating slowly in larger retorts increases the yield in oils and acetic acid and charcoal, but diminishes the yield of gas. Attaching the retorts to a vacuum pump during the process of distillation considerably increases the yield of volatile products. 100 parts air-dried wood yield on distillation:—

		Charcoal.	Tar.	Wood Vinegar.	Wood Vinegar containing Acetic Anhydride.	Gas.
Beech	slowly heated	26.7	5.9	45.8	5.2	21.7
	quickly ,,	21.9	4.9	39.5	3.9	33.8
Oak	slowly heated	34.7	3.7	44.3	4.1	17.2
	quickly ,,	27.7	3.2	42.0	3.4	27.0
Birch	slowly heated	29.2	5.5	45.6	5.6	19.7
	quickly ,,	21.5	3.2	39.7	4.4	35.6
Pine	slowly heated	30.3	4.4	41.0	2.7	24.4
	quickly ,,	24.2	9.8	42.0	2.4	24.1

Stolze obtained the following numbers as the result of slow and very careful carbonisation:—

100 lbs.	Charcoal.	Tar.	Wood Vinegar.	Wood Vinegar containing Acetic Anhydride.	Gases. Cubic Yards.
Beech	24.6	9.5	44.0	3.9	10.8
Oak	26.1	9.1	43	7.7	10
Birch	24.4	8.6	44.9	8.9	9.8
Fir	26.6	11.9	42.3	4.2	12.5

Especially worthy of remark is the small percentage of acetic anhydride in the wood vinegar from the pine and fir, and the large amount of gas yielded by fir. This explains why distillers of yellow pine seldom save the pyroligneous acid or wood vinegar.

The tar of the pine and fir contains a considerable amount of turpentine oils.

Fig. 146 shows a plant for wood distillation designed by the firm F. H. Meyer, Hannover-Hainholz. It consists of two iron cylinders A and B each about 3 m. long and 1 m. diameter imbedded in masonry and heated by means of a fire c placed intermediately between them. The hot gas and flame from the fire circulate round the retorts and slowly char the wood. The non-condensible gases coming over with the products of distillation pass from the condenser *g* through the tube *hi* and are burned as fuel under the retorts. The temperature is initially kept as low as possible. Up to 150° C. the distillate consists principally of water; between 150°-280° C. the bulk of the acetic acid and methyl alcohol comes over; above 300° C. tar distils. The gas escaping consists at first mainly of CO_2; at a higher temperature CO, CH_4, and H_2 gas comes over. Heavy gaseous hydrocarbons are hardly produced at all as with coal. The gases burn with a pale non-luminous flame. Immediately connected with the retort is a wide tube *e* leading to a tar separator, followed by a coil of copper tubes *f*, cooled by water in a tank. Here the liquid distillate condenses and can be run off into a suitable receptacle.

The non-condensible gases from the retort first pass a hydraulic seal (as in gasworks) *g*—to prevent the flame striking back—before passing along *hi* to the furnace.

The wood, cut into pieces of a suitable length and thickness, is placed in the retort by means of a wire-work cage, which slides in and out of the retort. In larger retorts the wood is placed in wire cars mounted on wheels, which run on rails in and out of the furnace. Fig. 147, which represents a modern plant manufactured by F. H. Meyer of Hannover-Hainholz, Germany, shows the most general type of retort, which is used in large works both in America and on the Continent, and which is rapidly replacing the oven system. Sometimes a steam exhauster is attached to the outlet from the retort, whereby the yield of acetic acid is considerably increased, since the volatile vapours are thus sucked out from the retort before they have been decomposed by the hot walls and high temperature. Dry wood gives the best results.

The distillation lasts twelve hours. The charcoal is withdrawn in closed iron-plate cylinders and is allowed to cool.

A cubic metre dry beech, weighing 396 kg., yields approximately 122 kg. charcoal, 157 kg. wood vinegar (containing 18.5 kg. acetic acid, and 4.6 kg. methyl alcohol), 24 kg. wood tar of sp. gr. 1.08, 93 kg. of gases; while to carry out the distillation needs about 43.5 kg. coal to heat the furnace.

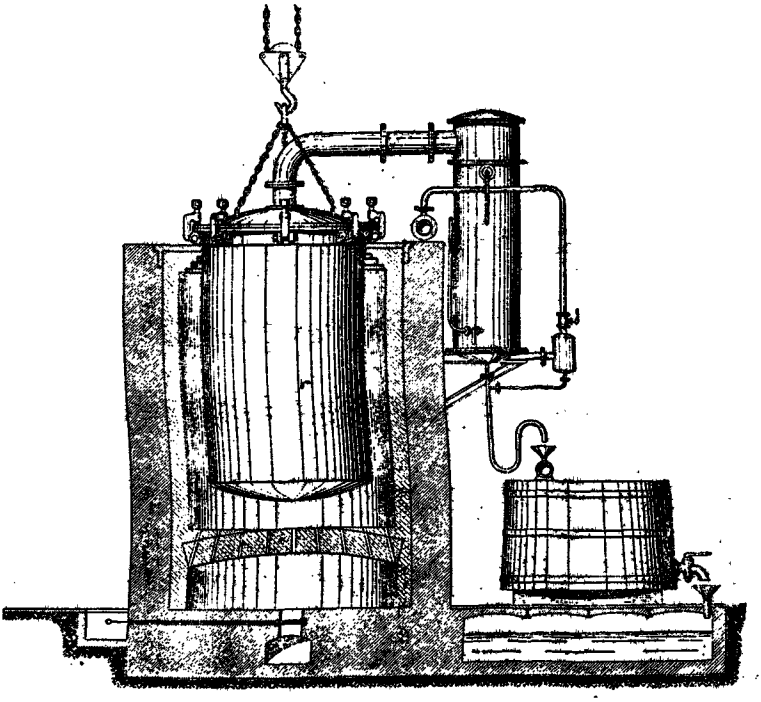

FIG. 148.—Vertical Retort.
(F. H. Meyer, Hannover-Hainholz, Germany.

When pine wood or fir containing much resin has to be distilled, usually *vertical* retorts are employed which contain at the bottom an outlet tube for the melted resin —a rather valuable product (Figs. 148, 149). Such retorts, although yielding better charcoal, are slightly dearer to work than horizontal retorts.

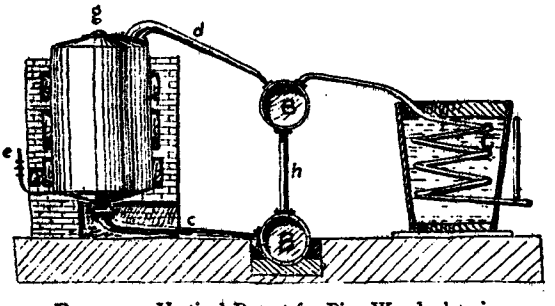

FIG. 149.—Vertical Retort for Pine Wood, showing Outlet Tube at bottom for Melted Resins.

Gröndal's Tunnel Kiln for Charring Wood (German Patent, 112,932, 18th July 1899).—The Iron and Steel Institute of Sweden in 1904 judged this system to be the best in use at that time; it is used at Pitkäranta in Finland. It consists of a masonry tunnel 66 m. long, divided into several compartments by dampers or doors of iron plate. The first compartment, 4.5 m. long, is the entrance chamber. Next comes the charring chamber, 40 m. long, followed by a 17 m. long "charcoal cooling" chamber, and finishing with another "entrance chamber" 4.5 m. long. Trucks on rails loaded with wood can be drawn through the tunnel. The central

charring chamber" is really a sort of muffle furnace, heated by the hot gases of furnace placed beneath the tunnel, the flames pass through earthenware or iron bes running round the interior of the chamber between the walls and the trucks, that the temperature is kept continuously high enough to completely carbonise wood. No gases from the fire, however, actually enter the chamber and come contact with the wood. The volatile products from the wood escape through es in the roof and are condensed in the ordinary way, as in the retort system. e tar in the wood drips from the cars on to the floor of the furnace, and runs depressions placed in the floor at intervals, thence escaping through pipes to ks placed on the outside of the furnace.

The wood, cut up into suitable slices, is loaded into wire-cage trucks and is ced in the furnace as follows: First the outer door of the entrance chamber is ened and a truck run in—the chamber being just big enough to hold it—and door is shut. Then all the sliding doors between the two entrance chambers e opened, and the whole row of trucks inside (filled with wood) are drawn through

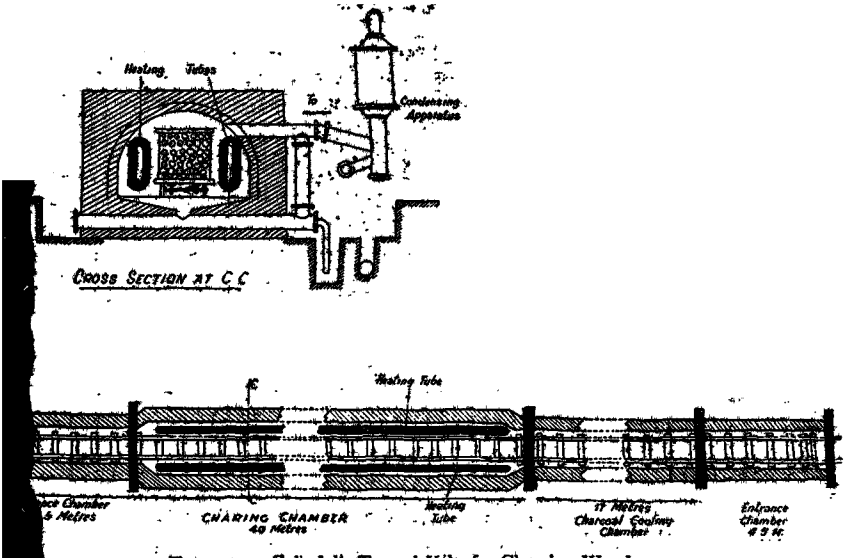

FIG. 150.—Grondal's Tunnel Kiln for Charring Wood.

n length by means of a winch placed outside the furnace. Consequently waggon in the furnace, which contains the charred wood or charcoal be removed, is drawn into the last entrance chamber, while the fresh uck is drawn from the first entrance chamber into the central charring . The furnace thus works, practically, continuously. Every hour a truck is drawn into the furnace at one end, and simultaneously, at the other end, f charcoal is withdrawn. The yield is stated to be less with this furnace ther constructions, but it is very suitable for countries rich in wood and uch charcoal.

Steam Distillation of Wood before Charring

Occasionally pine or fir wood rich in turpentine or resin is steam-distilled with saturated or superheated steam *before* carbonising, in order to recover the turpentine oil. The steam from a boiler passes through a superheater, and then in succession through two or more retorts. The melted-out liquid resins flow away from the

floors of the retorts, while the distilled products pass over to a condenser. Th wood is left dry—using superheated steam—and is then charred in the usual way.

Before charring the wood is sometimes extracted with solvents to recover rosi left in the wood; see under **Turpentine Industry**, p. 338.

Distillation of Sawdust and Wood Waste

Sawdust is difficult to distil in ordinary retorts owing to the fact that it is extraordinarily bad conductor of heat—so that the outer portions char before t internal layers are scarcely hot. Moreover, the charcoal formed is of little va since it will not form a coherent mass. Various devices are used, such as revolvi iron retorts, through the interior of which flames play. Halliday's apparatus, mu used in England, consists of a cylinder with a feeding screw, placed in a furnac According to the speed with which the screw is driven, the wood can be expos for a shorter or longer time to the action of the heat. Thus, as large as possib a yield of acetic acid is obtained (Fig. 151).

WOOD TAR AND PYROLIGNEOUS LIQUOR

The liquor distilling over from the retorts in which the wood is being carbonise separates out into: (1) **Wood Tar**, (2) **An Aqueous Layer called Py ligneous Liquor** (or c wood vinegar).

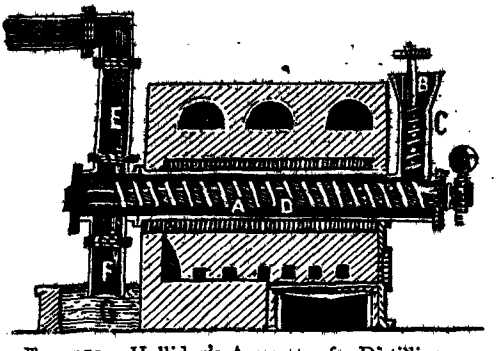

FIG. 151.—Halliday's Apparatus for Distilling Sawdust and Wood Waste.

Some very important improve in the separation of tar from the ligneous acid were made by th F. H. Meyer, Hannover-Hainh 1904 (see German Patents, Nos. 1 and 193,382). To effect a tech complete separation of tar fro pyroligneous liquor, they attach retorts a special condensing app (Fig. 152). The gases from the ch retorts enter at T and pass into a ber A which is heated to a suitabl perature by the live steam coil A the bulk of the tar condenses t with some acetic acid. The however, is again volatilised steam issuing from the coil *e*. vapours—already relatively ta rise up through A and pass into a successive series of chambers through bell capsules *b*, further condensation of tar takes place and the vapours passing through become still richer acid. The process is repeated in the successive chambers B, C, D, E, and the vapours escaping from E are practically free from tar, and on condensation and neutralisation wit directly yield grey 82 per cent. acetate of lime. The separated tar, pouring down thro tubes *a*, *a*, *a*, runs away at the base through a special outlet.

Wood Tar

Treatment of the Wood Tar.—The wood tar is run off from the layer of pyroligneous liquor and specially worked up. It contains an e number of substances, such as paraffins and other hydrocarbons, high phenols and their esters (but only a small amount of phenol, C_6H_5OH) paracresol, guaiacol, $C_6H_4\langle^{OH}_{OCH_3}$, kreosol, $C_6H_3(CH_3)\langle^{OH}_{OCH_3}$, pyrogall fatty acids and esters, and pitch.

Pine-Wood tar contains much turpentine.

Beechwood-Wood tar is especially rich in guaiacol and kreosol.

The so-called "Stockholm Tar"—principally from pine wood—is much valued as a preserving paint for ships, roofing, masonry, etc.

Distillation of Wood Tar.—Wood tar is distilled in a manner similar to coal tar, using the same precautions against boiling over. It is then separated into **Light Tar Oils, Heavy Tar Oils,** and **Pitch.** The **Light Tar Oils** are used much in the same way as **Benzine.** The lighter oils from **pine tar** are known as "Pine Oil," and are especially rich in **turpentine**; it is largely used for making paints, varnishes, and lacs. The more mobile part of **birch** tar, known as "Birch Tar Oil," is used in finishing **Russian leather.**

The **Heavy Tar Oils** (oil of pitch) are largely used in pharmacy and for

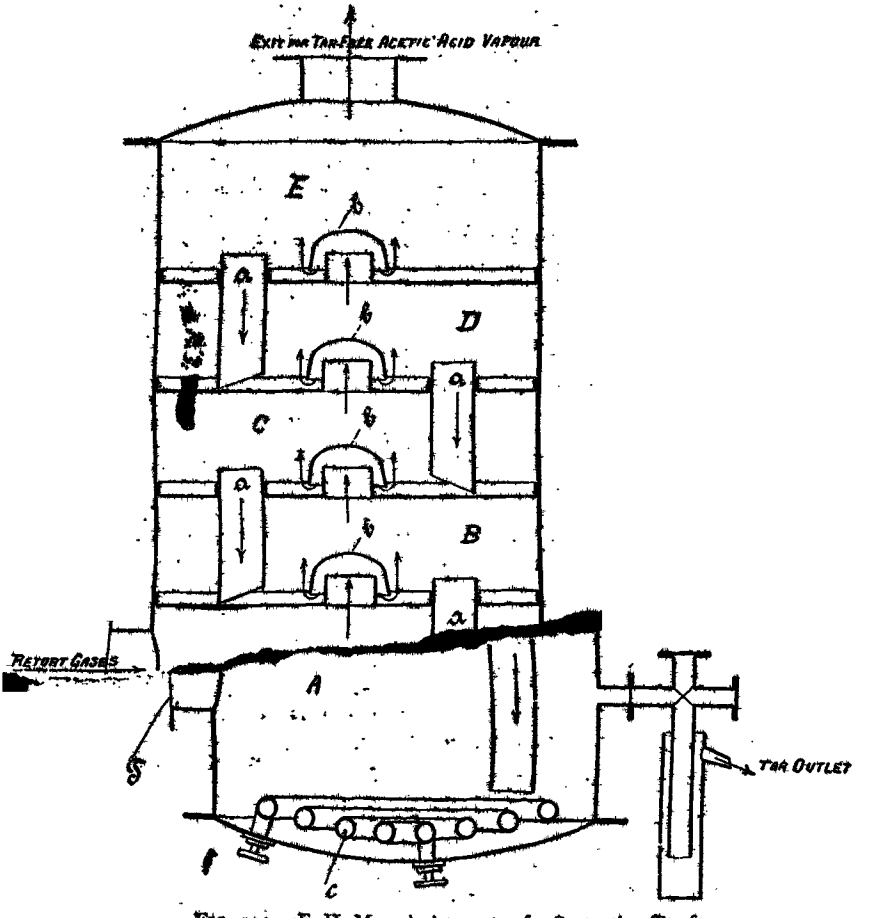

FIG. 152.—F. H. Meyer's Apparatus for Separating Tar from Pyroligneous Liquors.

egnating wood, etc., being more suitable for the latter purpose than the corre-ing oils from coal tar.

reosote is obtained from **beechwood** heavy tar oils by extracting with da solution, and precipitating with CO_2 or acid.

reosote boils between 200°-220° C., has a sp. gr. 1.07, and has a strong ur. It consists principally of **guaiacol** and **kreosol**, and is used: "quick smoking" process for ham, fish, etc.; (2) as an antiseptic in

medicine, being considerably less poisonous than phenol; (3) in medicine, especially for coughs, colds, consumption, etc. etc. Some of the "Pine Tablets," etc., placed on the market consist largely of these substances.

Pure **Guaiacol**, $C_6H_4(OH)(OCH_3)$ (1 : 2), isolated by means of its potassium or barium salt, is obtained in large colourless needles, B.P. 205° C. It is also produced synthetically, *e.g.*, by heating pyrocatechin with KOH and potassium methyl sulphate to 180° C.

Wood pitch, the residue left in the still, is mixed with coal tar or colophony asphalt, and sold for shoemaking.

Statistics.—England imported (principally from Russia) in 1910 about 279,600 cwt. of wood tar, of value £87,500. The United States in 1910 imported 1,018 barrels (280 lbs. to the barrel) of tar and wood pitch.

Pyroligneous Liquor or Crude Wood Vinegar.

The aqueous layer of pyroligneous liquor separated from the coal tar (above, p. 328) contains about 10 per cent. acetic acid, 1-2 per cent. methyl alcohol, 0.1-0.5 per cent. acetone, as well as small amounts of propionic, butyric, formic, and other acids, methyl acetate, allyl alcohol, furfurol, phenols, amines, ketones, etc. Suspended or dissolved in the aqueous fluid occurs about 10 per cent. of tarry matter.

Treatment of the Pyroligneous Liquor.—The liquor is distilled in order to separate the acetic acid, methyl alcohol, and tarry matter. The crude wood vinegar is placed in a vessel and boiled by means of a steam coil. The distillate passes in succession into two boilers, each charged with milk of lime. Here the acetic acid is fixed by the lime forming **calcium acetate**, while the methyl alcohol, passing on, is fractionated and condensed in a still. Any methyl acetate distilling is saponified by the lime into methyl alcohol and acetic acid.

A great saving in fuel, steam, and space is effected by F. H. Meyer's system (German Patent, 93,382) of distilling the pyroligneous acid in multiple evaporators in vacuum.

Manufacture of Acetate of Lime.—The contents of the boilers co
ning excess of lime and calcium acetate (which is in solution), are run
the solution evaporated with continual stirring in steam-heated copp
filtered, ing to the surface is skimmed off through a slidi
pans. The tarry matter rising ium acetate separates as
door. When the specific gravity reaches 1.110, the [illegible] dried contin
thick paste, which is removed and spread on flat iron pans to be dried, continually stirring the while with iron shovels. The "grey" acetate contains 80-82 per cent. calcium acetate and 20 per cent. water (from which it cannot be freed without decomposition).

Uses.—As a source of acetic acid, acetates, and acetone. Used in **Waterproofing**, p. 526.

Statistics.—The *export* of acetate of lime from the United States is shown by the following figures: 1906, 31,000 tons; 1910, 28,000 tons; value in 1910, $1,423,000.

The English import of acetate of lime (almost entirely from Canada and the United States) 1910 amounted to 4,300 tons (value £42,000). Germany produces about 10,000 tons.

Manufacture of Concentrated or Glacial Acetic Acid

S. MIERZINSKI.—"Die Industrie der Essigsäure u. d. essigsäueren Salze." Leipzig, 1905.

Glacial acetic acid is now manufactured almost entirely from the crude calcium acetate obtained from wood distillation plant (see above).

The method adopted is to decompose the calcium acetate with conc sulphuric acid, when acetic acid of 70-75 per cent. distils over mixed with other gases. 100 parts 80 per cent. calcium acetate are placed in cast-i provided with powerful stirring apparatus and heated by steam. Abo

ent. sulphuric acid are slowly run in and the distillation carried out in (see Lindes' German Patent, 92,418, 29th November 1894). The acetic distilling over is condensed in copper or earthenware tubes, while non-ensible evil-smelling gases pass on and are led into the furnace. A considerable nt of SO_2 escapes while part remains dissolved in the acetic acid. A mass lcium sulphate mixed with charred carbonaceous matter remains in the boiler. rude 70-75 per cent. acetic acid thus obtained (containing 0.1 per cent. SO_2) n fractionated from copper (or chamotte-plated cast-iron) boilers, using a ar condenser as in spirit distillation.

till is heated with steam and is coated internally with chamotte plates (since acetic acid esence of air attacks copper). The vapours pass out into a rectifying column, usually entirely out of porcelain or other acid-fast material, the outer casing being, however, In a water tank at the top of the rectifying column lies the **dephlegmater** (see under **llation**), which dephlegmates the dilute acid coming over at first. Later, when the id distils, the dephlegmater is disconnected. The first runnings consist of dilute acetic g SO_2, then the bulk of the practically pure acetic acid distils over, followed finally nologous acids, such as **propionic** and **butyric** acid. The glacial acetic acid is finally ling potassium permanganate and rectifying, using silver condensing coils.

Fabrik Rhenania (German Patent, 117,539, 8th March 1898) obtains a very pure cid by decomposing calcium acetate by means of sodium polysulphate, $NaH_3(SO_4)_2$ s a by-product in manufacturing nitric acid, German Patent, 106,962, 8th March 1898), a reflux condenser, when the reaction—

$$3Ca(C_2H_3O_2)_2 + 2NaH_3(SO_4)_2 = 3CaSO_4 + Na_2SO_4 + 6CH_3.COOH,$$

place. The product is free from H_2SO_4 and SO_2, and needs only rectifying once.

A. & J. Behrens (German Patent, 121,199, 6th October 1899) dissolve the commercial r cent. dry calcium acetate in 60 per cent. acetic acid, and add the theoretical amount of er cent. H_2SO_4. The $CaSO_4$ precipitating abstracts the water from the acetic acid $SO_4+2H_2O=CaSO_4.2H_2O$), and the whole mass becomes solid, when the concentrated acetic l is pressed over in the cold, or simply distilled.

Properties.—Pure 100 per cent. glacial acetic acid melts at 17° C., boils at 118° C.; technical glacial acetic acid contains 96-99 per cent. of acid. The pure acid should not decolourise potassium permanganate. On diluting with water the specific gravity *increases*, attaining a maximum density with an 80 per cent. acid; thereafter it diminishes, as the following table shows:—

Acetic Acid. Weight per Cent.	Sp. Gr. 15/4° C.	Acetic Acid, Weight per Cent.	Sp. Gr. 15/4° C.
100	1.0553	40	1.0523
90	1.0713	30	1.0412
80	1.0748	20	1.0284
70	1.0733	10	1.0142
60	1.0685	0	0.9992
50	1.0615		

Statistics.—Germany produces about 10,000 tons (at 550 m.) annually, 3,000 tons of which go in the manufacture of synthetic indigo (see this). England in 1910 imported 4,500 tons (value, £88,000).

Uses.—Largely used in coal-tar colour manufacture. The manufacture of synthetic indigo alone uses up over 3,000 tons yearly. The preparation of mordants—such as aluminium acetate, iron acetate, chromium acetate, copper acetate—for the cloth-dyeing and printing trades uses up very large amounts of acetic acid. The great value of acetate mordants lies in the fact that the acid is volatile, and on steaming escapes, leaving behind the sesquioxides of the metals. They are usually produced in solution in the dye vats by decomposing lead or calcium acetate with the sulphates of the required metals, the lead or calcium being precipitated as sulphate.

Crude acetic acid is used for smoking meat and fish. **Pure** acetic acid from wood is also used largely in Germany and France as a **table vinegar**, being flavoured for the purpose by digesting with certain aromatic herbs, such as fennel, being sold in a 70 per cent. solution as "Essence of Vinegar." See also **Vinegar**, p. 317.

Salts

Lead Acetate, "Sugar of Lead." $Pb(C_2H_3O_2)_2.3H_2O$, is obtained by dissolving litharge, PbO, in crude acetic acid or vinegar. The aqueous solution takes up more lead oxide forming basic acetates. Crystallises well.

Calcium Acetate, $Ca(C_2H_3O_2)_2.H_2O$, is an easily soluble body, but forms c... difficulty (see p. 330).

Sodium Acetate, $Na(C_2H_3O_2).3H_2O$, forms an easily soluble crystalline salt.

Copper Acetate (Verdigris), $Cu(C_2H_3O_2)_2.H_2O$, used as a paint (see **Pigments**).

Iron Acetate solution is obtained by dissolving scrap iron in crude acetic acid. Use... mordant.

For **Esters** of acetic acid see under **Alcohol Preparations.**

Monochloracetic acid, $CH_2Cl.COOH$, M.P. 62°, is now prepare... very large scale for the manufacture of synthetic indigo, by passing chlorine ... hot glacial acetic acid in the presence of acetic anhydride.

Methyl Alcohol, Wood Spirit

The crude methyl alcohol collected during the distillation of the p... liquid (see p. 330) contains about 10 per cent. methyl alcohol. It is r... milk of lime in a columnar still, and is thus placed on the market as ... "Crude Wood Spirit"; this contains as impurities allyl alcohol, ac... formaldehyde, furfurol, methylethylketone, acetone, amines, pyridine, etc...

It is purified by diluting to 30-40 per cent., adding milk of lime (20-30... every 1,000 l. of spirit), and carefully and slowly rectifying from large colu... stills for several days. The first runnings contain 8-60 per cent. acetone, and ... allyl alcohol; while the final fractions contain high boiling ketones, and are k... as "wood oil"—a practically valueless by-product. The intermediate frac... consist of nearly pure methyl alcohol, which is obtained practically pure by a... diluting with water, adding some NaOH, and rectifying. Last traces of acet... may be removed by distilling over bleaching powder, which converts the aceto... into chloroform, but at the same time destroys some of the methyl alcohol. Da... coloured, sharp-smelling impurities are often removed by filtering through woo... charcoal.

Properties.—Pure **methyl alcohol,** CH_3OH, boils at 66° C., has sp. gr. 0.80, and has a faint, spirituous odour. Taken internally it intoxicates, but is too dear for use as a spirituous liquor.

Uses.—Pure acetone-free methyl alcohol is much used in the colour industry for making dimethylaniline, methyl chloride, CH_3Cl, methyl bromide, CH_3Br, and

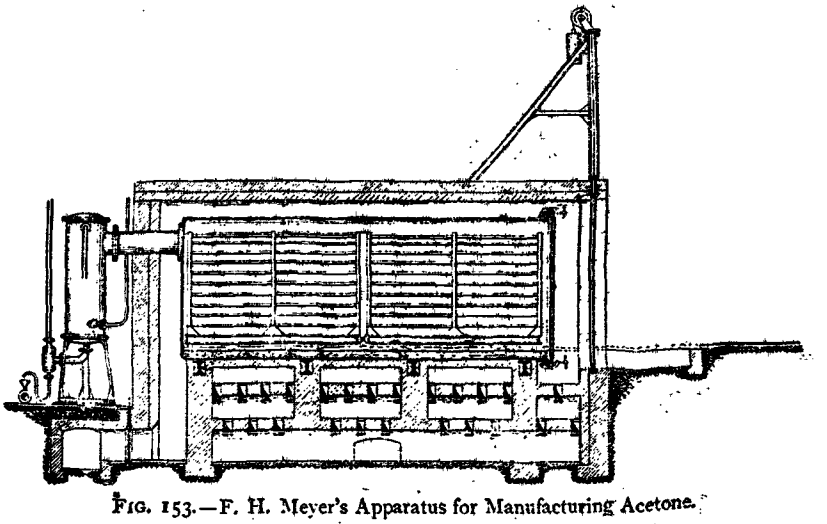

FIG. 153.—F. H. Meyer's Apparatus for Manufacturing Acetone.

[redacted] compounds. Crude wood spirit containing acetone and [redacted] has a sharp, aromatic smell and taste, and is used for denaturing al[cohol] (thus producing "Methylated Spirits") as well as for varnish making, F[rench] polishing, etc.

The source of methyl alcohol is invariably **wood**. The amount of aceto[ne] contains is determined by the **Iodoform Test**. (See **Acetone**.)

Statistics.—Germany in 1905 imported 4,770 tons at 700 m. from North America Austria. England in 1910 imported 448,500 gals. (value, £47,000), of which no less t[han] 400,000 gals. came fro... the United States. The *export* of wood alcohol from the United St[ates] is shown by the following figures: 1906, 780,000 gals.; 1907, 2,150,000 gals.; 1908, 1,959,000 ga[ls.] 1909, 1,100,000 gals.; 1910, 1,329,000 gals.; value in 1910, $582,000.

Acetone, Dimethylketone, $CH_3.CO.CH_3$, is a clear, mobile, ethereal-smelli[ng] liquid, boiling at 56.5° C., and of sp. gr. 0.797 at 15° C. Although it occurs [in] crude wood spirit it is seldom isolated from it, being used in the impure state f[or] denaturing alcohol. Pure acetone is manufactured on F. H. Meyer's system b[y] heating crude calcium acetate to 300°-400° in perforated trucks placed in a reto[rt] (Fig. 153):—$Ca(CH_3COO)_2 = (CH_3)_2CO + CaCO_3$. The volatile acetone vapours escape through a pipe and are condensed. There remains in the truck finely powdered $CaCO_3$, which is removed by opening the retort and running out the truck. The crude acetone contains homologous acetones and acids, as well as aldehyde, while CH_4 escapes. The acetone is purified by fractionating over lime. 100 kg. of 80 per cent. calcium acetate yield 25-30 kg. crude acetone of 60-70 per cent. Tralles. 100 parts of wood yield about 1 part of acetone.

Up to 1912 the sole source of acetone was the dry distillation of wood and the subsequent decomposition of calcium acetate. Owing to the modern use of wood pulp for paper, and the consequent diminution in the supply of wood available for destructive distillation, coupled with the low yield of acetone (only 1 per cent. of the weight of the wood), the supply of acetone was not meeting the rapidly increasing demand, and so the price had been rising until in 1912 it reached £89 per ton. In that year *A. Fernbach* introduced his **Fermentation Process** for producing acetone from starch. Grain, potato, or other starchy mashes are inoculated with Fernbach's culture, and allowed to ferment. The starch breaks down into higher alcohols (principally butyl) and ketones, of which acetone forms a considerable portion. The mashes are then distilled, and the acetone separated by fractional distillation. It is found that 15-20 per cent. of the starch is transformed into acetone. The crude starch acetone contained 78 per cent. pure acetone, 11 per cent. of "Miscible Ketones," and 11 per cent. impure acetone. The Synthetic Products Company of London propose to place the acetone on the market by this process at £35-£45 per ton (see p. 314).

Uses of Acetone.—Acetone is a valuable product employed for making chloroform (p. 378), iodoform (p. 380), and as a solvent for acetylene (pp. 401, 403); in making celluloid (p. 208), and synthetic drugs (p. 605). By far the greater quantity, however, is employed as a solvent for nitrocellulose in the manufacture of blasting materials and smokeless powders, such as cordite (see p. 639).

For explosive manufacture the acetone must be free from all acid or aldehyde, boil at the correct temperature, and yield with iodine and caustic soda solution the correct amount of iodoform, according to the equation:—

$$\underset{\text{Acetone (1 molecule).}}{(CH_3)_2CO} + 3I_2 + 4NaOH = 3NaI + \underset{\substack{\text{Iodoform}\\\text{(1 molecule).}}}{CHI_3} + Na(C_2H_3O_2) + 3H_2O.$$

Statistics.—The English import of acetone in 1910 amounted to 22,000 cwt., of value £57,000. The world's supply of acetone in 1912 was estimated at 10,000 tons.

SECTION VII

The Turpentine and Rosin Industry

THE TURPENTINE AND ROSIN INDUSTRY

By G. Martin, Ph.D., M.Sc.

LITERATURE

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...IL of Turpentine, or **Spirits of Turpentine**, is derived from coniferous trees ...pecially from the pine, *Pinus palustris*, and *P. Taeda*, L., and from the Scotch fir, *sylvestris*, L. Incisions are made in the bark of the trees, and the exuding ...scid liquid is caught in vessels placed beneath the cut. The substance is then ...acuum distilled in a current of steam. The volatile turpentine oils (forming about ...17 per cent. of the mass) distil over and are collected. There remains in the boiler ...the non-volatile colophony, which is run off. A modern plant is shown in the diagram, Fig. 154.

The crude resin is placed in a receptacle provided with a wire-net filter. It is melted by means of heat supplied by steam passing through the double bottom with which the receptacle is provided. Simultaneously a vacuum is set up in the still A by means of a vacuum pump. The melted resin is then strained through the wire netting and enters the still A through *a*. Here, under a vacuum of 15-25 cm. and at a temperature of 175°-185° C., the volatile oils distil over. The still may be placed over a fire, but is shielded from its direct action. It is often heated by gas or merely by superheated steam.

A steam coil *cc* containing superheated steam maintains the contents in ebullition, while at the same time a current of superheated steam is driven by means of the injector *mn* through the boiling oil. The volatile distillate condenses in the copper ...ils immersed in the water tank C, and runs into ...cting tank D, which is connected with ...cuating apparatus; as D fills the liquid is ...into another reservoir. When the distillation is finished the fluid colophony is run off ...A and allowed to solidify in suitable receptacles.

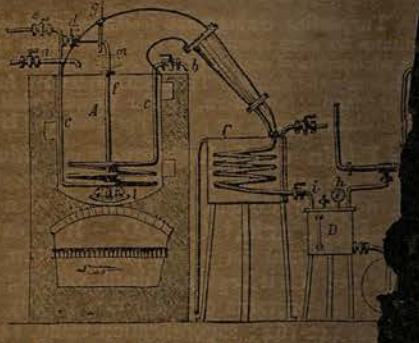


Fig. 154.—Krämer & Flammer's Vacu... Still for Rosin.

...e various turpentine oils consist of a number of isomeric **hydrocarbo...** ...e, $C_{10}H_{16}$; B.P. 155°-160° C., and of sp. gr. 0.85-0.87. The various bran... distinguished by their different degrees of optical activity. The th... ...mercial grades are important:—

...1. **French Turpentine**, consisting principally of the terpene "tereben... ...laevopinene," which is *laevo-rotatory* to polarised light.

2. **American or English Turpentine** contains the terpene, **Austr**[illegible] $C_{10}H_{16}$, which, as regards specific gravity, boiling point, and chemical properties, strongly resembles terebenthene, but is *dextro-rotatory*.

3. **Russian Turpentine**, which contains the terpene sylvestrine and another pinene (see under **Essential Oils**).

The oil of turpentine, after distilling, is washed with caustic soda solution to retain any rosin acids. It is then redistilled and sold as "rectified spirits of turpentine." It then forms a water-white, mobile, light refracting liquid, of sp. gr. 0.640-0.872, distilling between 156°-170° C. Exposed to air it absorbs oxygen and becomes resinous.

Much turpentine is made in Russia by the destructive distillation of twigs and leaves. Turpentine being such an extremely important body, repeated efforts have been made to extract it from twigs, branches, and felled timber by various processes, such as superheated steam or solvents. One of the most promising processes is that in which the wood is heated to 325°-375° F. in a bath of rosin, washed pine tar, pine oil, soft pitch, or the heavy residuum remaining after the distillation of the lighter oils obtained from wood. The solvent extracts the turpentine and similar products from the wood, and is then drawn off from it and superheated steam is then blown through the hot rosin bath, thereby distilling over the turpentine oils. Wood so treated is especially useful for making creosoted timber or street paving blocks. Many modifications of the process are known. For some recent patents see English Patents, Nos. 4,355, 1903; 15,338, 1906; 6,831, 1907; 5,0[illegible] 1906; 19,109, 1909; 29,886, 1909; 27,076, 1910. See also pp. 327-328.

A great improvement in the rosin industry was effected by G. Walker in 1905. The turpent[illegible] is first extracted by grinding the wood and submitting it to the action of live steam in closed vess[illegible] whereby the turpentine oil is carried over by the steam into a condenser and afterwards is refin[illegible] nd sold as wood turpentine. Next the wood is treated in a kind of Soxhlet extractor for the recove[illegible] of the rosin still in the wood. In an apparatus erected by Walker at Conway, S. Carolina, abo[illegible] 200 barrels of rosin are produced per week, together with much turpentine. The process produc[illegible] five times as much rosin and turpentine in twelve hours as the same quantity of wood produces [illegible] four years by the old method of boxing the trees, and so will probably supersede the older methods.[1]

Turpentine is one of the best and most widely used solvents for resins and oils in making varnishes and paints. The disinfectant **Sanitas** is stated to be made by passing a current of air through **Russian turpentine** in the presence of **warm water**.

Turpentine Substitutes (communicated by Mr Dancaster, B.Sc.).—The chief turpentine substitutes are rosin spirit, shale spirit, petroleum spirit, and coal-tar naphtha. All these may be used as adulterants of real turpentine or as substitutes for the latter. Also the cheaper kinds are used to adulterate the dearer. These substitutes are frequently sold under fancy names such as "turpentyne," and "turpenteen." For **Rosin Spirit**, see below. For **Shale Spirit**, see p. 8. For **Petroleum Spirit**, see p. 7. For **Coal-Tar Naphtha**, see p. 417.

Rosin or Colophony, the residue left in the still after the turpentine oil has been removed, is one of the cheapest resins (see p. 349), occurring as a yellowish or brown brittle mass. It consists of a mixture of modifications of the anhydride of **abietic acid**,† $C_{20}H_{40}O_2$. It is extensively used for making varnishes, soap, lin oils, and for sizing paper, cotton, etc. It is stable at 150° C., but between 250°-300° C. it begins to distil, yielding **rosin spirit** and **rosin oils** (which see). The constants of rosin vary greatly with its source and quality; neutralisation [illegible]e, 140-164; saponification value, 147-176; iod. value, 90-180.

Destructive Distillation of Rosin.—By carrying the distillation of rosin [illegible]colophony further than is required to separate turpentine oil, it is decom[illegible] ween 250°-300° C., yielding a number of oils.

The colophony is placed in a large iron still, capable of holding 50-70 barrels of ros[illegible] ated by direct fire. The still is connected with a suitable copper condenser and the o[illegible] es about twenty-four hours. There finally remains in the still a coal-like mass. Dur[illegible] structive distillation a considerable quantity of gas is evolved, which is led into the furnac[illegible] nt as fuel under the still.

[1] See Pritchard, "Recent Developments in Wood Distillation," *Journ. Soc. Chem. Ind.*,

† The formula of abietic acid is variously given by different writers. A common formul[illegible]

The first distillate is a pale yellow oil, known as **rosin spirit**, boiling between 78°-250° C., and consisting of a complex mixture of hydrocarbons and oxygenated bodies, and somewhat resembling turpentine, for which it is sometimes substituted.

The distillate is washed with sulphuric acid to remove alkaline impurities, and then with caustic soda to remove acid impurities. It is then redistilled. Refined rosin spirit is a colourless, light, volatile liquid of unpleasant odour. Its specific gravity varies from 0.876-0.883. On exposure to the air it evaporates, but a portion oxidises to a resinous solid, in the same manner, but to a lesser extent, as turpentine. The spirit consists of principally various hydrocarbons, among which amylene, C_5H_{10}, hexylene, C_6H_{12}, and heptine, C_7H_{12}, have been found. When of good quality rosin spirit is the best substitute known for turpentine. Its composition, however—and therefore its quality—is very variable, and it frequently contains rosin oil, which prevents the proper drying of the paint with which it is used. It is sometimes adulterated with shale or petroleum spirit.

Rosin Oil, produced by the destructive distillation of rosin, comprises the bulk of the distillate; B.P. 300°-400° C.; sp. gr. 0.982-0.988; iodine value, 112°-115°. Probably consists of a mixture of **abietic acid**, $C_{20}H_{40}O_2$, phenols, and complex hydrocarbons, $(C_{10}H_{16})_2$, boiling above 360° C. Rosin oil is used as adulterant for olive oil, boiled linseed oil, etc., also as a lubricant for iron rings. It unites with alkalis to form greasy bodies, the compound with lime, $(C_{10}H_{16})_2.Ca(OH)_2$, being the commercial "Rosin Grease."

Resin Oil is a pale yellow oil obtained after the turpentine is removed from the crude turpentine obtained by distilling wood; B.P. 200°-214°. According to Harper ["Utilisation of Wood Waste," p. 127 (1907)] it consists principally of turpineol, $C_{10}H_{17}OH$.

Statistics of the Turpentine Industry.—The English import of turpentine oil in 1910 was 3,600 tons (value, £1,000,000). Of this quantity 18,000 tons came from U.S.A. The import of rosin was 75,000 tons (value, £880,582). The United States of America produce yearly nearly £4,000,000 of turpentine oil and colophony. In 1905 Germany imported 26,200 tons of oil of turpentine and rosin oils (value, £1,000,000) and 73,540 tons of rosin (value £500,000).

The following figures show the magnitude of the United States *export*:—

	1906.	1910.	Value in 1910.
Rosin - - - -	2,439,000 barrels *	2,144,000 barrels*	$9,753,000
Tar, turpentine, and pitch	...	40,000 ,,	148,000
Spirits of turpentine -	15,981,000 gals.	15,588,000 gals.	8,780,000

Acknowledgment.—My best thanks are due to Mr W. H. Stephens, A.R.C.S., for much information regarding recent processes for extracting turpentine; also to Mr Dancaster, B.Sc., chemist, L. & S.W. Railway, for information regarding turpentine substitutes, rosin spirit, shale spirit, etc.

* 280 lbs. to the barrel.

APPENDIX

NATURAL AND SYNTHETIC CAMPHOR

By G. Martin, Ph.D., M.Sc.

LITERATURE

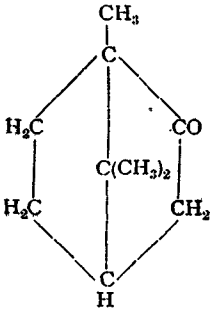
For Patent Literature relating to Camphor, see Winther's "Patente der Organischen Chemie." 3 vols. 1877-1905.

Camphor, $C_{10}H_{16}O$, is contained in the ethereal oil of the camphor tree, *Laurus camphora*, of China and Japan. It is obtained by boiling the finely divided wood with water, when the camphor floats to the surface, and on cooling solidifies. Sometimes the wood is steam-distilled. It is refined by mixing with carbon and quicklime and subliming.

Properties.—White crystalline solid, characteristic odour, burning taste, almost insoluble in H_2O, readily soluble in alcohol, ether, chloroform, etc. Sp. gr. 0.922-0.995; M.P. 175°; B.P. 204°. Tough, but may be easily powdered after moistening with alcohol.

Isoborneol, or **Borneol** (Borneo, Sumatra camphor), is allied to camphor, and may be converted into it by oxidisation (see below).

Uses of Camphor.—Principally for making **celluloid** (which see), also in Medicine, as a moth-preventative, in fireworks and night-lights.



Camphor (Bredt).

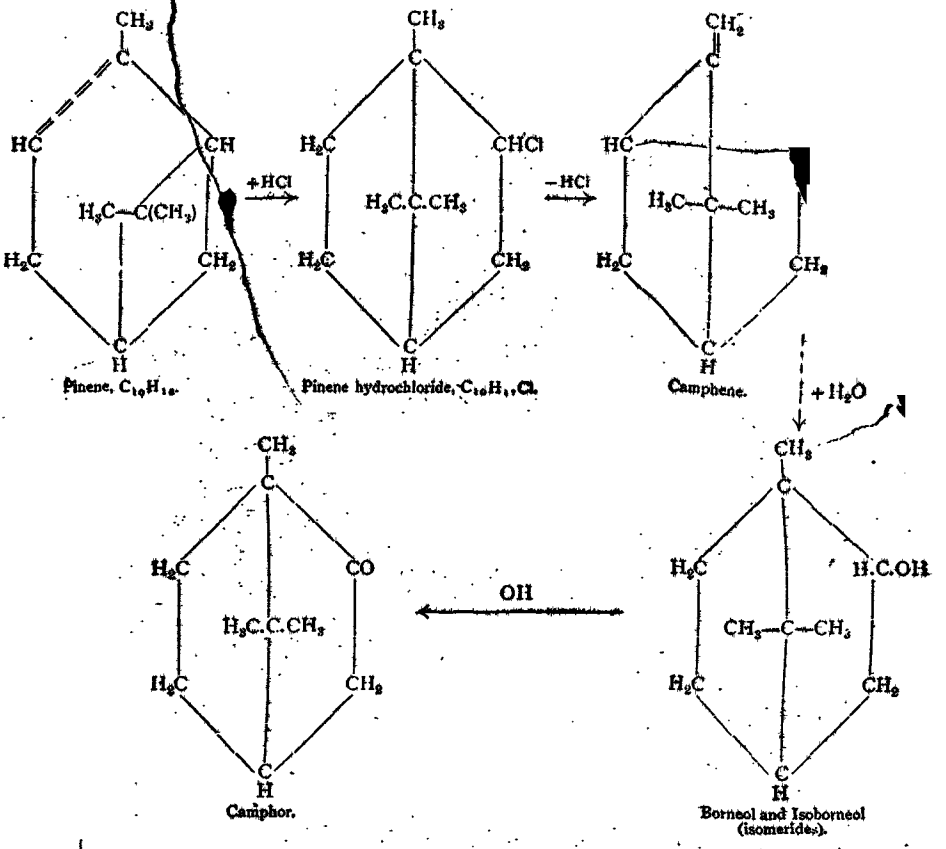
Synthetic Camphor.—Since Bredt established the constitution of camphor, numerous attempts have been made to produce it synthetically, and with considerable success.

The starting point is **pinene**, $C_{10}H_{16}$, a terpene hydrocarbon, which may be obtained pure by the fractional distillation of turpentine oil.

Two main types of process for synthetic camphor manufacture exist, viz., those which proceed by converting **pinene** into a HCl derivative, and those which treat pinene with organic acids.

1. Dry **HCl** gas is led into dry pinene, and the white solid product pinenehydrochloride, $C_{10}H_{17}Cl$, is isolated. The **Cl** atom is removed by heating with alkaline reagents, when a hydrocarbon, $C_{10}H_{16}$, camphene, is obtained. This when treated with the lower fatty acids + a little HCl, forms an ester of isoborneol and also (a little) of borneol, $C_{10}H_{18}O$. Next the isoborneol and borneol is obtained from the ester by saponifying, and converted into camphor by gentle oxidation. The yield of camphor from solid pinenehydrochloride may amount to 95 per cent. of the theory.

The following scheme shows the main chemical changes which take place:—



The literature dealing with the chemical changes involved is enormous, and the number of processes patented for carrying out the various stages is very large.

The first firm to manufacture synthetical camphor was the *Chemische Fabrik auf Aktien* (vorm. Schering) of Berlin, who possess a whole series of patents. Other firms are following suit. Among the more important recent patents we may mention German Patents, 149,791, 153,924, 154,107, 185,042 and French Patent, 349,896, 1904, which deal with the conversion of pinenehydrochloride into camphene. The German Patent, 67,255 (expired 1901), of Bertram (conversion of camphene into the ester of isoborneols and borneols by heating with acetic acid + a little concentrated H_2SO_4 below 50° C. and saponifying resulting ester with production of borneol and isoborneol) is the most important one for the production of borneol and isoborneol from camphene. Other patents are German Patent, 178,934 (uses fatty acid salts or aromatic carboxy acids ipstead of acetic acid), English Patent, 5,549, 1904, and French Patent, 349,852, (1904), convert pinenehydrochloride direct into borneol and isoborneol by heating it for ten hours at 120° in an autoclave with an alcoholic solution of NaOH + Na formate.

The oxidation of borneol and isoborneol is covered by numerous patents, such usual agents as air, oxygen, ozone, chlorine, nitric acid, $KMnO_4$, etc. etc., being used. By treating camphene with ozone, Richardson (English Patent, 3,555, 1896) and Nordheim (German Patent, 64,180) convert camphene directly into camphor with a yield of 80 per cent. theory.

2. **Pinene** (or turpentine oil) is heated at 100° C. for thirty-six hours with acetic acid, when borneol acetate is obtained (see Bouchardat and Lafont, *Comp. rend.* (1886), 102, 171). This on saponifying yields borneol and isoborneol, which are then converted into camphor by oxidation as before.

The yield is bad by this method: such products as limonene, dipentene, and others, are generated from the pinene. Hence, although the method is extraordinarily simple, the methods comprised under (1) still hold the field. Repeated attempts have been made to improve the yield; for example, the German Patents, 175,097, 178,934 (Chemische Fabrik von Heyden), use salicylic acid, of acetic, for heating with pinene; anhydrous oxalic acid is proposed in the American P... 761, and German Patent, 134,553—the yield amounting to 35 per cent. theory.

...mphor monopoly, which the Japanese Government established after the ... of Formosa, has been broken down by the manufacture of synthetic

...stics.—The United States in 1910 imported 3,027,000 lbs. (value $922,000) of crude ...or, and 477,000 lbs. (value $180,000) of refined or synthetic camphor.

SECTION VIII

Industrial Gums and Resins

INDUSTRIAL GUMS AND RESINS

By J. Newton Friend, D.Sc., Ph.D

LITERATURE

For Rosin (Colophony) see under **The Turpentine Industry**, p. 337.
For Resins and Gums see Andés, "Die Harzprodukte." Vienna, 1905.
Andés.—"Gummi Arabicum." Vienna, 1896.
Cordenoy.—"Gommes, Résines." Paris, 1900.
„ "Plantes a Gommes et a Résines." Paris, 1911.
Friend.—"Introduction to the Chemistry of Paints." Longmans & Co., 1910.
Lutz.—"Études chemique des Gommes." 1895.
Tschirch.—"Die Harze und die Harzbehalter." Leipzig, 1906.
Dieterich.—"Analysis of Resins, Balsams, and Gum Resins." London, 1901.

It is customary to use the term "gums" and "resins" synonymously, but this is a mistake. Strictly speaking, gums are those extudations of trees and plants generally that are either entirely or partially soluble in water, yielding sticky masses from which they are precipitated on the addition of alcohol. They are, therefore, used in the preparation of the so-called water varnishes, and are introduced into distempers on account of their binding properties. Resins, on the other hand, are insoluble in water, but usually dissolve in organic solvents such as alcohol, benzene, and turpentine. Clearly, therefore, it is incorrect to include benzoin and the dammars amongst the gums, and equally wrong to classify gum arabic and gum tragacanth as resins. It is not always easy to draw a sharp line of demarcation between gums and resins, but for all practical purposes it is well to bear the above distinction between gums and resins clearly in mind.

Broadly speaking, resins are brittle and lustrous. The Sierra Leone and Pebble copals are particularly good cases in point, being much prized by varnish manufacturers. Few of the varnish resins possess any distinctive odour, benzoin constituting the main exception, its pleasant aromatic perfume being familiar to all who have to deal with resins.

For the preparation of clear and colourless varnishes the palest resins are in great demand, and therefore fetch the highest prices. This is one of the reasons why cheap varnishes are darker and less transparent than those for which a higher price is paid.

We have already remarked that resins are soluble in organic solvents, but towards these reagents their reactions are both curious and interesting. Thus, for example, rosin and sandarac readily dissolve in alcohol, benzene, and turpentine, and are worked into varnishes with relative ease. Some of the other resins are insoluble in all the usual vehicles until after they have been fused by heat. This is true for the copals, and considerably enhances the difficulty and therefore the cost of manufacturing varnishes from them. As we shall see presently these peculiarities afford a very valuable means of identifying and distinguishing the resins.

Statistics.—The following figures show the value of the various gums and resins imported into the United Kingdom :—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Gum arabic	77,000	107,400	£176,000
,, kowrie	128,000	157,000	638,000
,, lac-dye, seedlac, shellac, and sticklac	82,300	174,000	627,600
Other gums and resins	213,500	223,200	559,000

The United Kingdom exported in 1910 about 27,000 cwt. of British-prepared gums (value, £68,000).

The United States *import* of industrial gums and resins is given by the following figures:—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Gum arabic	36,200	48,000	$315,000
Chicle	50,400	60,600	2,547,000
Copal, kauri, and dammar	182,600	262,100	2,962,000
Gambier or terra japonica	279,200	228,300	1,256,000
Shellac	140,000	262,500	3,878,000
Tragacanth	...	12,000	310,000
All other	...	...	1,445,000

The export (principally to Canada) was in 1910: *Gum arabic*, 2,000 cwt. (value $18,000); *chicle*, 15,000 cwt. ($565,000); *copal and kauri*, 12,000 cwt. ($165,000); *gambier*, 7,000 cwt. ($41,000); *shellac*, 3,900 cwt. ($84,000); all other, $72,000.

GUMS

Gum Arabic or **gum acacia** exudes from many plants, chiefly varieties of acacias growing throughout Australia, Asia, and Africa. As practically none of it comes from Arabia the term Arabic is unfortunate. The gum is essentially the calcium and potassium salts of arabic acid, and, by the addition of hydrochloric acid and alcohol to the aqueous solution of the gum, a fairly pure specimen of arabic acid may be obtained as a white amorphous mass to which the formula $(C_6H_{10}O_5)_2H_2O$ is usually given.

Different specimens of the gum vary considerably in colour, the palest fetching the highest prices. Good qualities require only one and a half times their weight of water to effect their complete solution into a sticky mucilage of great value to stationers. Boiling with dilute sulphuric acid converts it into galactose.

When starch is gently warmed with dilute hydrochloric acid it yields a sticky fluid known as **British Gum** or **Dextrine** which is used as a substitute for gum arabic. It is usually prepared commercially by moistening starch with 2 per cent. nitric acid, and, after allowing it to dry in the air, heating the product to 150° C. (See p. 184 for manufacture.) When boiled with dilute sulphuric acid it yields *d*-glucose.

Gum Tragacanth is a different type of gum from the above, in that it is insoluble in cold water, and swells in hot water to a mucilaginous liquid that cannot be filtered. It is procured from several species of **astralagus**—a group of trees growing on the east of the Mediterranean.

Chicle is a Central American gum obtained from the white sap of gum-producing trees. It is first allowed to oxidise, then melted in a special rough oven of native manufacture, and the product so obtained is flavoured with brown sugar, coloured with stains, slightly flavoured with various flavouring materials, and then exported chiefly to America for use as a chewing gum.

Tragasol.—This gum is very similar in all respects to the pharmaceutical gum tragacanth. It is mostly used as a binding material, and in America tragasol is often sold as Tragacanth. Said to be used for carrying colour. American import in 1910 was 1,183,000 lbs. (value $24,000).

Gambier.—Gambier is an extract obtained from leaves and small branches which grow on the islands in the East Indies. In commerce it occurs in brown earthy masses, and is imported chiefly from Singapore. It is used in medicine as an astringent, and is also employed by tanners and dyers.

RESINS

The resins in common use are more numerous than the gums. We shall deal with them here in alphabetical order.

Amber is one of the most highly prized and valuable resins, having been used from the earliest times for ornamental purposes. Amber is found on the shores of the Baltic Sea, and it is also dug out of beds or mines in Germany, Poland, and certain parts of America. It is occasionally found on the Norfolk coast in this country, and has been picked up as far north as Sandsend and Whitby in Yorkshire. Its occurrence on our coasts is, however, too uncertain to render a British amber trade possible.

Amber is the resinous exudation of certain pine trees that existed ages ago, and are now probably extinct. At one time it must have been soft and viscous, for the remains of insects and vegetable matter are frequently found embedded in it. The largest piece of amber on record is that numbered amongst the royal jewels at Berlin in Germany, and weighs no less than 18 lbs.

As a varnish resin amber is very valuable, since it yields a varnish that offers a stout resistance to the action of the atmosphere. Unfortunately, however, its expense prevents its being used as much as would otherwise be the case.

It may be taken as an axiom that all good things are liable to unworthy imitation, and amber is no exception to the rule. It is not infrequently adulterated with common rosin or colophony, and, in order to increase the deception, insects and organic matter are introduced into the mass. Fortunately, however, adulteration of this kind is readily discovered in a variety of ways. For example, whilst amber melts at about 600°-615° F. (316°-324° C.), the adulterated product has a much lower melting point. It is useful to remember that two pieces of genuine amber may be readily joined together after softening the ends in a solution of caustic potash, whereas no such fusion occurs with the fictitious product, or at any rate, only with difficulty.

The name **Animi** is given to a pale resin found in Zanzibar. Like amber it is a fossil, being found embedded in the surface soil, covered with a reddish crust. When this is scraped off the characteristic "goose skin" appearance of the pure resin is laid bare. It is an excellent varnish resin, and is used in the manufacture of the best quality of coach varnishes.

A somewhat similar resin is collected by Arabs from certain trees direct, and goes by the name of "recent" or "virgin" animi. It is inferior to the true or fossil animi, and finds application in the manufacture of poorer qualities of varnish.

We have already had occasion to mention **Benzoin**, or "gum Benjamin," as it is frequently called, although, strictly speaking, it is not a gum. This resin is obtained from the *Styrax benzoin*, a tree growing in Sumatra and neighbouring islands. The tree is cultivated from seed, and in about seven years' time is ready for tapping. Each tree yields some 3 lbs. of crude resin annually, the product during the first few years being fragrant, soft, and pale. As the tree ages, however, the exudation becomes harder and too dark to be of service in varnish manufacture.

The properties of benzoin are subject to considerable variation according to the districts from which it is obtained. Thus, the Siamese product is brittle and

possessed of the strongest odour; whereas that from Sumatra is somewhat greyer in hue, less odoriferous, and possessed of a higher melting point.

Under the generic name **Copal** are included a large number of valuable varnish resins possessing a considerable variety of properties. Thus, some are soft, like the **Manilla copal**; others are hard and lustrous, the **Sierra Leone** and **Pebble copals** being cases in point; **Java copal** has a milky appearance; and so on. The bulk of the copals are obtained from Africa and America.

The various resins known as **Dammars** are found in India and the East Indies. **Batavian dammar** is used in the manufacture of coach and cabinet varnishes. Other varieties are known as **white, black, sal,** and **rock dammars** respectively.

An entirely different kind of resin from any hitherto mentioned is that known as **Dragon's Blood,** which is obtained from the dragon tree (*Calamus draco*) in Eastern Asia. To this end the fruit is allowed to ripen and the resin with which it is then covered is collected and cast into rolls approximately a foot long and an inch in diameter. As its name implies, it is possessed of a red hue, and is used in colouring or staining varnishes the same colour.

The term **Elemi** is generic like copal and dammar. The most important resin of this group, known as **Manilla elemi,** is obtained from the *Canarium commune*, a tree growing in the Philippine Islands. It finds application in the manufacture of varnish as a toughener.

Gamboge is obtained from the bruised leaves of a Siamese tree known as *Garcinia morella*. It is soluble in alcohol, and when taken as a medicine exerts a drastic purgative action upon the system. Like dragon's blood it is used for colouring varnishes, and water-colour artists employ it as a pigment.

Gum Accroides is the resinous secretion of certain Australian trees, and finds application in the manufacture of dark gold lacquers and yellow varnishes. The prefix "gum" is a misnomer.

One of the palest and most important of the New Zealand resins is known as **Kauri, Kowrie,** or **Cowrie**—a fossil occurring in the soil at various depths below the surface. It may also be obtained direct from living trees upon incision. In order to distinguish between the two varieties the latter is usually termed "young" kauri.

Of all the known resins, **Lac*** is one of the most useful. It has been known for centuries, and the lac industry is one of great importance, so much so that in 1907-08 the total export from India was valued at £2,665,224. Lac differs from the resins hitherto described in that it is not the ordinary secretion of a tree or group of trees, but is produced by small insects known as *Tachardia lacca*, which feed upon the trees and excrete the lac. No fewer than eighty-seven different species of tree are known in India upon which the lac insect grows wild. When in the larval or caterpillar stage, colonies of these insects puncture the bark of the tree and suck up the sap, excreting a resinous mass which forms a light yellow encrustation round their bodies. After a few weeks the larvæ have developed into perfect insects, both male and female, the latter greatly preponderating in point of numbers. After impregnation the females become distended with a red liquid known as **lac dye.** The lac is now collected, the twigs upon which the colonies had collected being broken off by the natives and termed **stick lac.** This is crushed and washed, whereby the bits of wood are separated, and the product is known as **seed lac.** Further washing removes the dye, which is a marketable product, and the lac is melted and ladled on to a revolving cylinder whereby it solidifies in the form of thin flakes of **shellac.** Sometimes it is allowed to solidify in thicker discs and finds its way into the market as **button lac.** The terms **lemon lac, orange lac,** and **garnet lac** refer to the colour of the product, and this is determined to some extent upon the tree from which it has been obtained. **White shellac** or **bleached lac** is the ordinary shellac which has been bleached.

* These remarks on lac have been culled from the interesting paper entitled "Technical Notes on Lac," read by A. F. Suter on 11th March 1909 before the Paint and Varnish Society.

Shellac is used largely in electrical work as an insulating material. It is also valuable for the preparation of knotting, varnish, etc.

Mastic is the exudation of the lentisc tree which flourishes by the Mediterranean. It is used in the preparation of picture varnish, and this, when mixed with linseed oil, constitutes megilp.

Hitherto we have used the word resin in a generic sense. Sometimes it is employed—but quite wrongly—to indicate the solid residue left behind in the stills after the extraction of the turpentine from the crude resinous exudation of the pine trees in France, America, and Russia. This product is really **rosin**, also known as colophony.

The best qualities of rosin are pale or amber coloured, and are used in making "finish" and the cheaper qualities of varnish. (See under **Turpentine Industry**.)

The last resin to be considered is **Gum Juniper** or **Sandarac**, which is obtained from certain North African trees. It is used in the manufacture of both spirit and oil varnishes, but in the latter case it must be first fused to render it soluble in the linseed oil.

For artificial resins see p. 211.

Identification of Gums and Resins

From a chemical point of view, gums, and particularly the resins, are extremely complex, so that an analysis in the ordinary sense of the term is not possible. When heated the gums char and the resins readily burn with a luminous, smoky flame, showing the presence of a considerable quantity of carbon. If, therefore, we wish to identify the substances we shall have to judge usually by the cumulative evidence of a series of tests. These may be conducted as follows: *—

1. **The Appearance.**—Dragon's blood, gamboge, and the lacs may be distinguished by their colour. Mastic is usually in the form of small tears of a pale yellow hue, which soften when placed in the mouth. This enables us to distinguish it from sandarac, the only other resin with which it is likely to be confused. The "goose skin" surface of animi and the pebbles of pebble copal are distinctive, as is also the odour of benzoin. Gum acacia may be recognised by its taste and its resinous appearance, and gum tragacanth by its peculiar flakes.

2. **The Specific Gravity.**—This usually varies within narrow limits only. Care must be taken, however, to use only such specimens as are free from air bubbles, otherwise too low a value will be obtained (see table, p. 350).

3. **The Melting Point.**—The appearance of the gum or resin during the whole process of heating should be noted, as this is frequently characteristic. Many resins have no definite melting point (see table, p. 350).

4. **Behaviour towards various Solvents.**—This is most conveniently ascertained by shaking up a small portion of the resin with a little of the solvent in a tube, warming if necessary.

(*a*) **Water.**—Gum acacia and British gum dissolve in both hot and cold water. Gum tragacanth swells in hot water only, and rosin forms a semi-fluid mass. Elemi, dammar, shellac, and mastic become sticky in hot water, but amber, copal, and sandarac remain unchanged.

(*b*) **Caustic Soda.**—Amber softens and its ends can be fused together. Rosin partially dissolves. Shellac and the gums readily dissolve.

(*c*) **Ammonia.**—Rosin and gamboge dissolve at once. Copal, mastic, and sandarac soften and slowly dissolve. Amber, dammar, elemi, and shellac are unaffected.

(*d*) **Sulphuric Acid.**—The gums yield sugars on boiling with the dilute acid. All the resins dissolve in concentrated sulphuric acid, yielding a dark brown solution, save dammar and benzoin which usually afford a reddish hue.

(*e*) **Carbon Bisulphide.**—Dammar and rosin dissolve with ease. Elemi, mastic, and sandarac dissolve slowly. Copal usually softens, but amber and shellac do not dissolve.

(*f*) **Boiling Linseed Oil.**—Amber and copal are indifferent. Elemi, sandarac, and shellac dissolve slowly. Dammar, mastic, and rosin readily dissolve.

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* It is here assumed, of course, that the gum or resin to be examined is one of those commonly occurring on the market and described in the preceding pages. It is usually exceedingly difficult and often impossible to identify with certainty the rarer specimens.

TABLE OF THE SPECIFIC GRAVITIES AND MELTING POINTS OF THE RESINS*

Name of Resin.	Specific Gravity.	Melting Point, ° F.	Melting Point, ° C.
Amber	0.98-1.20	600-615	316-324
Animi	1.04-1.07	450-465	232-241
Asphaltum—lake	1.38	189-210	87-99
,, land	1.43	210-255	99-124
Benzoin—Borneo	1.16-1.17	170-212	77-100
,, Penang	1.14-1.16	170-212	77-100
,, Siam	1.24	170-212	77-100
Copal—Angola	1.06	...	...
,, Demerara	1.03	450-465	232-241
,, Java	1.03-1.04	347	175
,, Manilla	1.06	230-250	110-121
,, Pebble	1.055	...	...
,, Sierra Leone	1.054	400	204
Dammar—Batavian	1.06	260-300	127-149
,, Black	1.09	...	...
,, Sal	1.10-1.12	...	...
,, Singapore	1.06-1.12	260-300	127-149
Dragon's blood	1.20	248	120
Elemi	1.02	170-250	77-121
Gamboge	1.03	...	...
Gum accroides	1.20	...	...
Kauri	1.05	360-450	182-232
Lac	1.10-1.20	...	...
Mastic	1.06	221-248	105-120
Rosin	1.04-1.10	117-212	47-100
Sandarac	1.04	300	149

* This table is compiled by kind permission of Messrs Longmans & Co. from Friend's "Introduction, etc.," p. 176.

(*g*) **Turpentine.**—Amber, shellac, and the gums are insoluble. Benzoin partially dissolves. Elemi, mastic, rosin, and sandarac dissolve easily.

(*h*) **Alcohol.**—Amber and the gums are insoluble. Dammar may partly dissolve, and copal becomes softened. Elemi dissolves with difficulty. Benzoin, gamboge, mastic, rosin, sandarac, and shellac readily dissolve.

(*i*) **Benzene.**—Amber, copal, shellac, and the gums are indifferent. Elemi and sandarac dissolve, but less readily than dammar, mastic, and rosin.

In applying these tests, however, it must be borne in mind that different samples of the same gums and resins are liable to show irregularities and slight variations in their properties, so that due care must be taken before conclusions are drawn.

SECTION IX

The Rubber Industry

THE RUBBER INDUSTRY

I.—NATURAL RUBBER, GUTTA-PERCHA, AND BALATA

(*For Synthetic Rubber, see p.* 366)

By A. J. Carrier, B.Sc.

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INDIA-RUBBER

General.—Indiarubber is nearly always obtained, in the first instance, as a milk (latex) which exists in the form of a negative emulsion (*i.e.*, the drops of rubber carry a negative charge) between the outer bark and the cambium, and which is coagulated and, if obtained from a plantation, washed and dried. This product is exported, and is subjected by the rubber manufacturer to a series of processes comprising further washing and drying, the "crepe" obtained being rendered plastic by heating and kneading (mastication) prior to adding vulcanising and other ingredients, where necessary. The mixture is now moulded by rolling, if for sheets, or into other forms, and is vulcanised. This is the process usually employed for "mechanical" goods.

Fig. 155.—Para Rubber Tree Thirty Years Old, showing Full Herring-Bone Tapping, Botanic Gardens, Singapore. (By kind permission of the Malay States Development Agency, London.)

Sources of Rubber

(*a*) **Euphorbiaceæ**—(1) *Hevea.* About 60 per cent. of the total output of rubber is obtained from the *Hevea braziliensis* of Para, Amazonas, and Brazil, which is the tree almost always grown on the Eastern plantations. It grows to a height of 100 ft., with a diameter up to 40 in. (2) *Manihot* (Brazil). The native allows the latex to coagulate naturally as it flows down the tree—it yields Maniçoba or Ceara scraps. (3) *Sapium* (Colombia) yields Colombia, Virgin, and Carthagena scraps. (4) *Urcandras* (Upper Amazon), mixed with Negro-heads, etc., from Para.

(*b*) **Apocynaceæ**—(1) *Funtumia* (tropical Africa), gives a rubber of high quality, known as Gold Coast Lumps, Ivory Coast Lumps, Niger Niggers, etc. (2) *Landolphia*, or Vine Rubbers (Congo, etc.) Best known brands are Red and Black Kassai, Upper Congo balls, Equateur, Madagascars (such as Virgin sheets, Pinky), and Sierra Leone Niggers. (3) *Clitandra* (Gold Coast and Congo). (4) *Hancornia* (Brazil), yields Mangobeira. (5) *Dyera* yields Jelutong, of which Palembang and Pontianac, or Dead Borneo, are the best known brands.

(*c*) **Urticareæ**—(1) *Ficus*, of which *Ficus elastica* or *Rambong* (Burmah, Ceylon, Malaya, Java, India, etc.), is the best known, and which yields brands known as Assam, Rangoon, Java, and Penang. (2) *Castilloa* (Mexico, Central America, etc.), yields Peruvian "Cancho," Cancho Negro, Mexican Strips, Centrals.

(*d*) **Compositæ.**—*Parthenium Argentatum Gray*, a shrub, yields Guayule.

From the latex of any of these species it is possible to prepare a dry rubber containing from 1.5 to 3 per cent. of resin for *Hevea*, *Castilloa*, and *Manihot*, and 5 to 7 per cent. for *Ficus*, *Funtumia*, and the better *Landolphias*, and not more than 3 to 5 per cent. jointly of ash, proteid, and other substances. However, many raw rubbers as imported contain admixed earth, bark, stones, etc.

It is doubtful whether any rubber is better suited for tyre covers and other articles subjected to shearing strains than *Manihot* and *Funtumia elastica*.

One system of "tapping" or obtaining latex, in use on Para plantations, is illustrated in Fig. 155, and consists in paring away, daily or on alternate days, a narrow strip of bark along the lower sides of a series of slanting cuts leading into a central cut, at the bottom of which a cup for receiving the latex is placed. When the bark has been removed over a sufficiently wide area, the tree is allowed a rest of some three or four years. The most general system of tapping is the "half herring-bone." The *Hevea* tree gives, per annum, some 2 to 3 lbs. of rubber for 150 to 160 tappings, the *Castilloa*, 1 lb. for 4 to 5 tappings.

Hevea trees should be over five years old before they are worked for rubber. In the case of smaller rubber shrubs, such as guayule, where tapping is inapplicable, the rubber is obtained by extracting with solvents or by mechanical processes in which the shrubs or the rich bark are pulped, and the pulp run into settling tanks; the rubber and a portion of the bark float on the surface. Guignet's process, which depends upon mechanical attrition and agglomeration of the rubber by friction, is described in British Patent Specifications, Nos. 18,375, 1910, and 9,064, 1909.*

Nature of Latex.—Latex consists of a fluid in which globular-shaped particles are suspended. These particles show typical "Brownian" movement, and wander to the anode if an electric current be passed through the latex, which may, therefore, be looked upon as a negative colloidal emulsion. This Brownian movement may be modified or caused to cease entirely by the addition of certain reagents, dilution, boiling, or by the electric current. Rubber latices contain, in addition to rubber, water, resins, proteid, mineral matter, peptones, sugars, simple albane-like oxygen derivatives, and various enzymes, such as oxydase, peroxydase, and catalase.

The following analyses give the composition of latex :—

	Seligmann.	Scott.	Bamber.
	Per Cent.	Per Cent.	Per Cent.
Water	55·56	52·32	55·15
Rubber	32	37·43	41.29
Protein and albumen	2-3	2.71	2.18
Resin	traces	3·44	...
Ashes (mineral substances)	...	0.23	0.41
Sugar	...	4.17	0.36
Oil	9.7	traces	...

* See also Patent Specifications, No. 23,682, 1912.

Coagulation.—1. The old process of coagulating by smoking on "paddles," still carried on in the Amazon district in the production of "fine Para," is as follows:—A fire producing dense smoke is made from *Urucuri* nuts, palm leaves, etc.; the

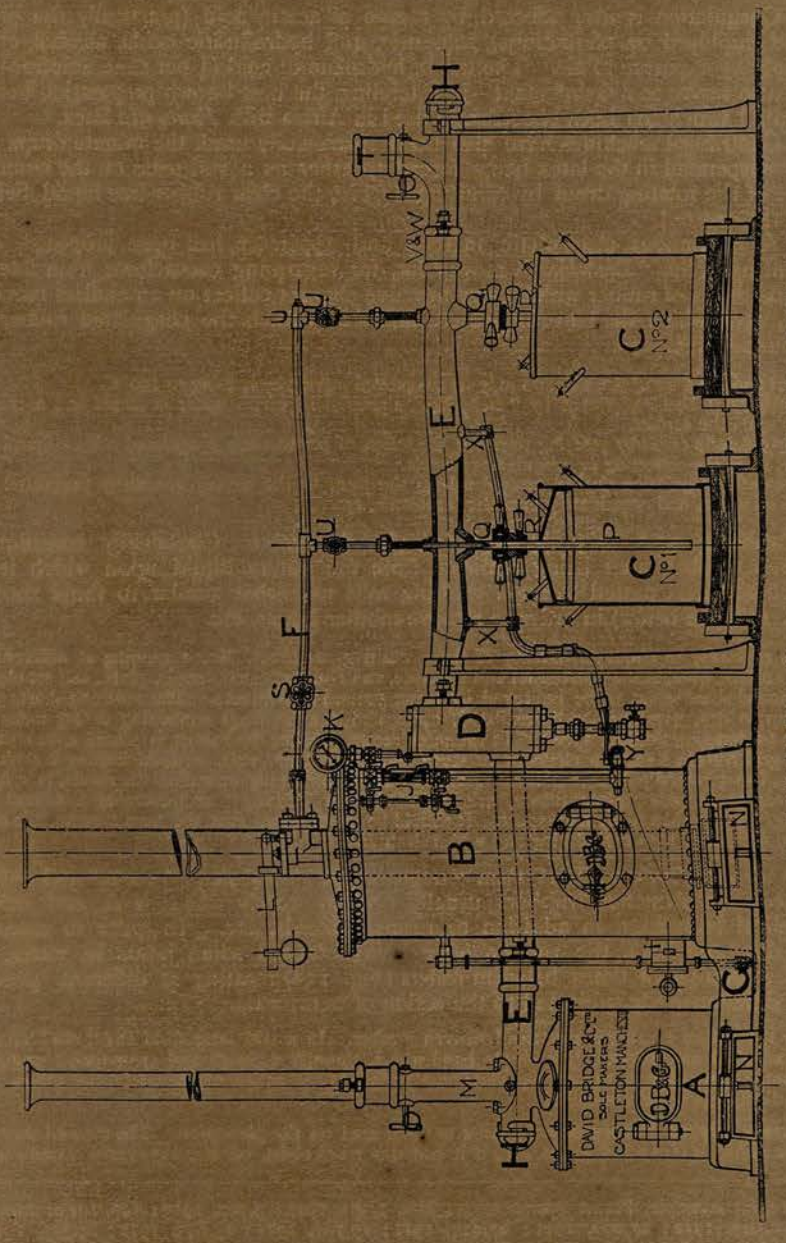

FIG. 156.—Da Costa's Rubber-Latex Coagulator. (David Bridge & Co., Manchester.)

paddle, after being coated with latex, is supported on a bar over, but not too near, the fire, and is rotated by hand until coagulation occurs. This process is repeated to build up a succession of films forming a ball of the desired size.

Various forms of apparatus for more efficient smoking have been recently suggested; the essential

points of which depend upon producing the smoke in an enclosed furnace, cleaning it by means of baffles, screens, etc., and then bubbling it with steam (Da Costa system) through the latex, or passing it over thin films of the latter upon travelling bands or rotating cylinders in closed chambers.* It remains to be seen, however, if these processes will result in such an excellent product as is "fine Para."

2. Coagulation is also affected by means of acetic acid (practically the only method employed on plantations), sulphuric, and hydrofluoric acids, alcohol, etc., or simply by exposure to air. The use of hydrofluoric acid (¼ per cent. solution)—which also serves as a disinfectant—is extending, the best known preparation being "Purub,"† which has been successfully used in Africa with *Funtumia* latex.

3. Centrifugal machines have also been successfully used, the minute drops of rubber suspended in the latex being forced together as a soft mass on the circumference of the rotating drum by centrifugal force, the clear rubber-free liquid being left in the centre.‡

4. A continuous electrolytic method and apparatus has been proposed, dependent upon the "Brownian" movement, for separating caoutchouc from latex.§ The fine drops of rubber which carry negative charges collect on an endless moving anode, upon which the latter is poured, and from which the coagulated rubber is continuously removed.

Funtumia and some other latices may be coagulated merely by heating to 100° C.

Castilloa is best coagulated by "creaming," a process in which water is added and a cream collects upon the surface.

Negro-heads result by pressing together the scraps of prematurely coagulated rubber found on the tree, or in the collecting or coagulating vessels.

Premature coagulation during transport from the trees to the factory is usually prevented by addition of water, and occasionally formalin, ammonia, etc.

Washing and Drying.—(1) *On the Plantation.* Chemically coagulated plantation rubber, after being removed from the watery liquid upon which it is found floating, is passed through washing rolls somewhat similar to those shown in Fig. 158 (see below) in order to remove mother liquor, etc.

It is advisable to employ a battery of three washing machines, No. 1 running at differential speeds and set wide, No. 2 differential and set close, and No. 3 at equal speeds, plain, and set close. The smoked sheet seems to be improved by being pressed into blocks. The resulting sheets are hung up to dry, usually in well-ventilated, corrugated-iron buildings containing drying racks or battens for hanging the sheets over. In the most recent practice the rubber is placed upon steam-heated grid coils in a vacuum chamber or stove, but, as a general rule, artificial heating is avoided because, if not carefully done, tackiness results. During the drying operation the sheets, or crêpe, of a creamy or pale yellow colour, are subjected to a "curing" or preserving treatment by smoking, and are then ready for export. It should be remembered that the term "curing" is also used synonymously with coagulating and with vulcanising.

(2) *In the Factory.* Fine Para "negro-heads," "biscuits," "worm," and other imported non-plantation rubbers usually contain woody fibre, sand, and other mechanical impurities, in addition to resins, proteids, etc. In order to remove sugar, dirt, and bark, the rubber, after being steeped some hours in water, is passed a number of times between rollers (Fig. 158) rotating at different speeds, and is simultaneously subjected to the action of warm water.

Fig. 158 shows a modern electrically-driven washer. In a still later form the "nip" of the rolls is adjusted and aligned by a single hand-wheel, through a clutch and cross-shaft‖ supplied from above. In order to expose the maximum surface to the action of the water, the rollers are usually diamond-cut, or corrugated.

Factory Drying Processes are similar to those used on the plantation. The cleaned sheet is dried on racks, or if of a low grade, *i.e.*, if it contains much resin, on canvas-covered frames, over

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* See, for example, Patent Specifications, Nos. 7,371, 1907; 3,703, 1913; 849, 1913; 23,219, 1912; 20,049, 1912; 27,666, 1911; 27,424, 1911; 19,784, 1911; 13,823, 1911; 24,325, 1910; 21,634, 1910; 19,730, 1910.

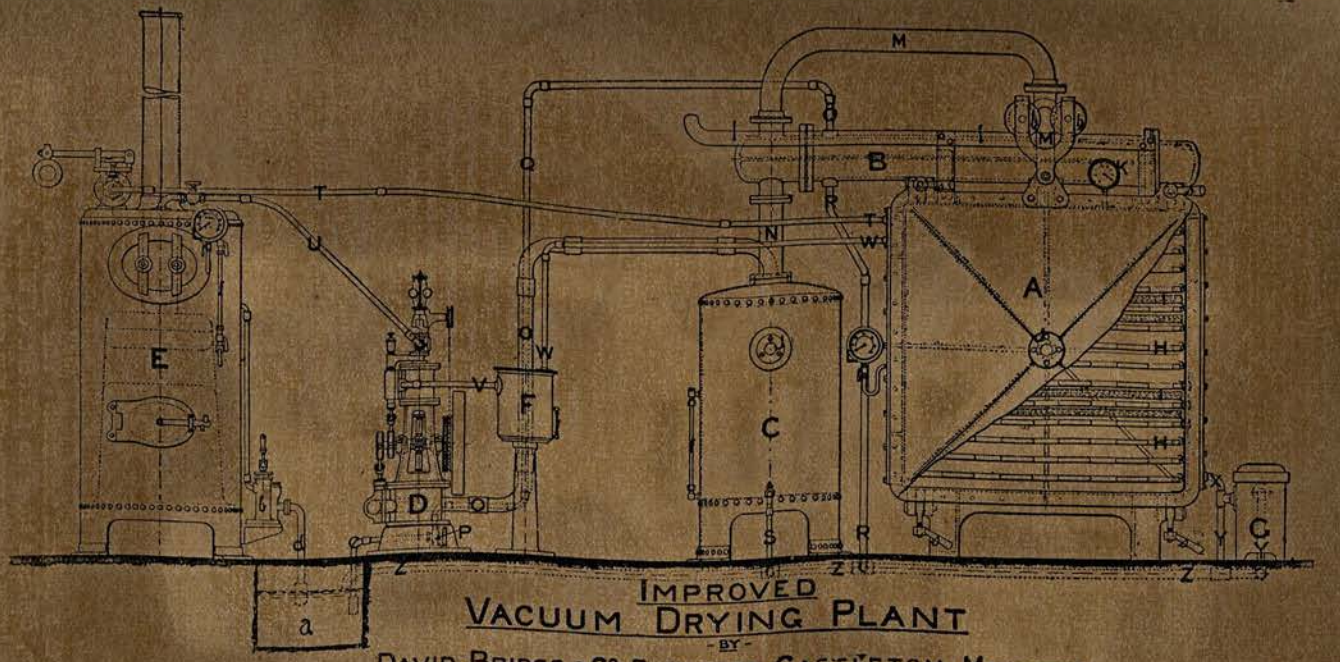
† See Patent Specification, No. 10,848, A.D. 1907.

‡ See Patent Specifications, Nos. 330, A.D. 1905, and 7,433, A.D. 1909.

§ See Patent Specifications, Nos. 21,441, A.D. 1908, and 5854, A.D. 1910.

‖ See Patent Specification, 28,781, 1911.

which a current of warm air is passed. The loss of weight occasioned by the combined washing and drying treatments is known as the "washing loss." In the case of "fine Para" this amounts to 12 to 20 per cent., and in the case of "Negro-heads" is sometimes as high as 40 per cent. The dry rubber is now ready for mastication or for mixing, which processes are described later.



IMPROVED
VACUUM DRYING PLANT
-BY-
DAVID BRIDGE & Co ENGINEERS CASTLETON MANCHESTER

A. Vacuum Chamber or Stove
B. Surface Condenser
C. Receiver
D. Steam-driven Air Pump
E. Steam Boiler
F. Oil Separator made under Baker's Patent
G. Steam Trap
H. Steam-heated Grid Coils
I. Galvanised Iron Wire Trays
J. Sight Glasses
K. Vacuum Gauge
L. Steam Gauge
M. Air Pipe from Stove to Condenser
N. Air Pipe from Condenser to Receiver
O. Air Pipe from Receiver to Air Pump
P. Water Circulating Pump
Q. Water Pipe to Condenser
R. Water Pipe from Condenser to Drain
S. Water Pipe from Receiver to Drain
T. Steam Pipe to Heating Grids in Stove
U. Steam Pipe to Engine
V. Exhaust Steam Pipe from Engine to Oil Separator
W. Exhaust Steam Pipe from Separator to Heating Grids in Stove
X. Exhaust Steam Pipe from Heating Grids to Steam Trap
Y. Exhaust Steam Pipe from Steam Trap to Drain
Z. Drain to Tank in Floor
a. Water Tank in Floor
b. Hand Boiler Feed pump
d. Suction Pipe. Tank to Pump
e. Suction Pipe. Tank to Circulating Pump
f. Water Gauge Glasses
h. Runners Carrying Door of Stove
l. Rail for Runners
s. Swing Bolts for Door of Stove.

NOTE.—The Stove Door partly broken away to show Interior.

FIG. 157.

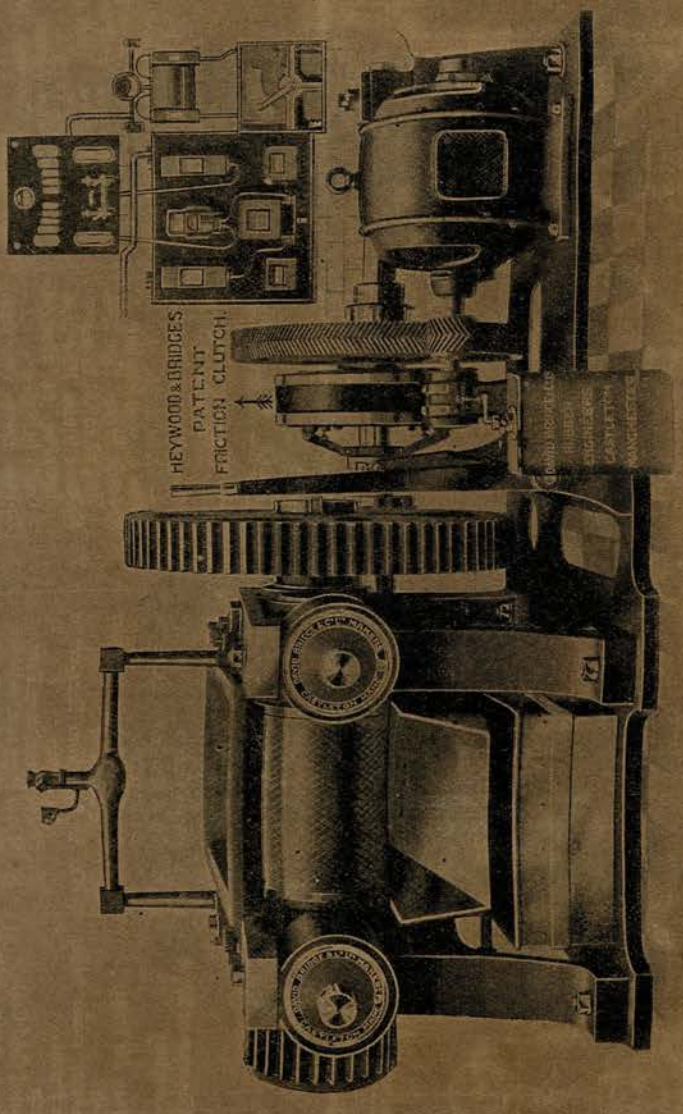
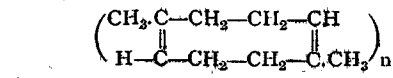


FIG. 158.—Washing Mill.

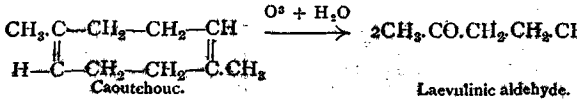
Jelutong is subjected to a different treatment. This gum in its crude state, as obtained after coagulation, contains some 10 per cent. of rubber, 60 to 70 per cent. of water, the remainder being chiefly resin, and was originally looked upon as a low grade rubber. A high grade rubber is now obtained from it by deresinating the washed gum, and it is often imported as dried and smoked crêpe.

Constitution and Properties of Caoutchouc.—Caoutchouc consists of a highly polymerised hydrocarbon of formula $[C_{10}H_{16}]_n$, mixed with some resin, proteid, mineral matter, etc.

According to *Harries** it contains an eight-ringed carbon chain, thus :—



He bases this conclusion on the fact that he succeeded in combining the rubber molecule with ozone, thus producing the ozonide $C_{10}H_{16}(O_3)_2$, which with water split up into laevulinic aldehyde and a superoxide of laevulinic aldehyde :—



Caoutchouc. Laevulinic aldehyde.

Rubber when hydrolysed yields ozonides, laevulinic acid, and laevulinic aldehyde. A current of air passed through a warm benzine solution yields $C_{10}H_{16}O$ and $C_{10}H_{16}O_2$. Cl and I acting on a $CHCl_3$ solution yield $C_{10}H_{14}Cl_2$ and $C_{10}H_{16}I_2$ respectively, but it is doubtful whether these are definite compounds. Bromine derivatives are $C_{10}H_{16}Br_4$, $C_{10}H_{15}Br_5$. Various nitrosite and nitrosate compounds have been prepared; for example, with nitrous acid caoutchouc in benzine solution forms a yellow nitrosite, $C_{10}H_{15}N_2O_7$. When distilled, caoutchouc yields a mixture of **isoprene** (C_5H_8 or $CH_2=C(CH_3)-CH=CH_2$), B.P. 37° C., and dipentene, $C_{10}H_{16}$, B.P. 171° C. And conversely caoutchouc may be artificially produced by the polymerisation of **isoprene**, which has been industrially produced on the large scale for the manufacture of synthetic rubber.

According to Harries, caoutchouc is produced by the condensation of pentose sugars contained in the plant, just as starch and cellulose are produced from the condensation of hexose sugars. In other words, rubber is a multiple of the hemiterpene group, C_5H_8, just as cellulose and starch are multiples of the hexose groups, $C_6H_{10}O_5$. Harries showed that Para rubber exists in three forms, an oily, the ordinary soluble form, and an insoluble modification.

Under ordinary pressures fine Para melts about 188° C. to a gummy mass, simultaneously undergoing decomposition as does vulcanised rubber when melted. Under high pressures, however, and in the absence of air, vulcanised rubber may be melted to a fluid mass and heated to higher temperatures than 400° F. without decomposition or loss of elasticity on cooling. Advantage is taken of this fact in the regeneration of rubber (see later). Unvulcanised caoutchouc is characterised first by its extraordinary elasticity at 15°-20° C., and secondly, by its plasticity at 50° C., so that when warmed it can be pressed into any shape and intimately mixed by kneading with other substances. At 0° C. it becomes hard. Freshly-cut surfaces of unvulcanised rubber may be made to adhere to one another at ordinary temperatures without using a solvent. The specific gravity of latex is about 0.976; of freshly coagulated rubber, which shows a reticulated structure, about 0.91-0.926. Raw rubber absorbs water and increases in volume.

"**Tackiness**" in raw rubber is an abnormal condition. The following causes have been observed or suggested: Sunlight, heat, bacteria, enzymes, faulty coagulation, small quantities of specific chemical substances, absence of moisture, and the presence of excessive moisture.

Vulcanised as compared with raw rubber is stronger, more resilient, more elastic, more stable towards actinic rays, solvents, and reagents, less changeable under variations of temperature, *e.g.*, it does not harden on moderate cooling, or soften under moderate heating, and is not adhesive. It is only slightly attacked by alkalies or dilute acids, unless, of course, it contains fillers which are acted upon by these reagents; conc. H_2SO_4, or HNO_3, and oils readily attack it.

The perishing † of rubber, which is hastened by exposure to strong light and warmth (say 50°-70° C.) is usually due to oxidation, which results in the formation of resinous compounds and traces of sulphuric acid; and to faulty curing resulting in "after-vulcanisation" if an excess of free sulphur be present. It has recently been shown that soft rubber changes but slightly if kept in the dark at ordinary temperatures, whether wet or dry. The effect of light on rubber is of great importance in connection with balloon fabrics. V. Henri, as the result of recent experiments, came

* See *Harries*, "Ber.," 37 (1904), 2,708; 38 (1905), 1,195, 1,198, 3,985, 3,989.

† W. O. Ostwald and Walter Oswald (Patent Specification, 10,361, 1910) claim a process for regulating the changes produced by auto-oxidation and polymerisation in rubber, etc., by treating it with neutral and basic aromatic nitrogen compounds, or neutral and basic heterocyclic substances or alkaloids (see p. 361, "Accelerators").

to the conclusions that crude rubber should not be used in balloon work, and that the cloth employed and the rubber should be coloured with a ultra-violet screen, such as chrome yellow. A high grade soft rubber breaks at about ten times its original length, and the load at breaking will be about 10 tons to the square inch, *i.e.*, since rubber is practically incompressible, 1 ton to the square inch of the original section. A well-made rubber buffer may be compressed many thousand times to about one-third its original thickness without lasting effect.

The extension curve of a good rubber shows a reversal of sign, usually at double the original length, accompanied by a flattening of the curve.

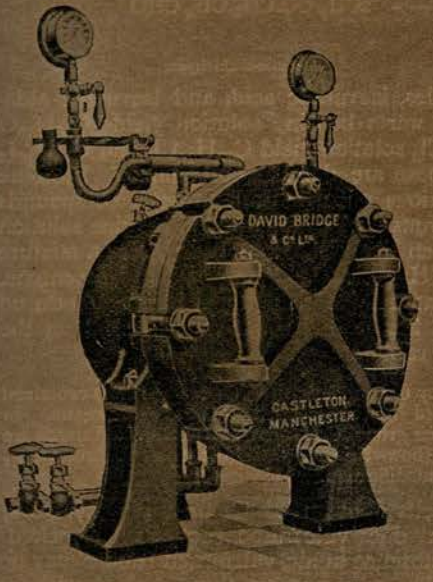


FIG. 159.—Vulcaniser Closed.

Solvents for Rubber.—Unvulcanised rubber swells up, however, when mixed with solvent naphtha, benzol, benzine, carbon bisulphide, carbon tetrachloride, chloroform, petroleum-ether, benzaldehyde, camphene, oil of turpentine, caoutchoucine (dipentene), etc., and forms what may be termed "colloidal solutions," as distinguished from true solution—the rubber having a sponge or foam-like structure, and the solvent, diffusing in by osmose between the walls, distends the rubber network into what we call a "solution." A solution is more easily obtained by treating the rubber immediately after mastication.

Spence and Kratz (*Kolloid Zeitschrift*, xiv., p. 262, 1914) found that the addition of small quantities of some acids greatly facilitates the solution of raw rubber, thus with the addition of 0.3-0.5 g. of $CCl_3.COOH$, 100 g. of dry washed rubber could be dissolved in 1,000 c.c. of C_6H_6 in the *cold in forty-eight hours*.

Patents cover the production of

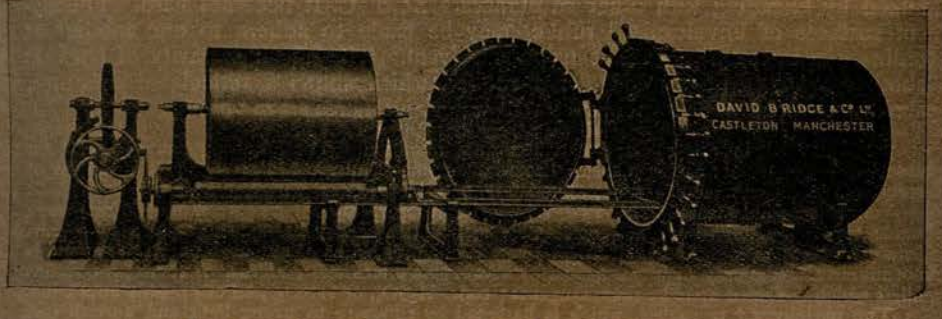


FIG. 160.—Vulcaniser Open. (David Bridge, Manchester.)

non-inflammable solutions by using carbon tetrachloride, dichlor-methane, tri- and tetra-chlor ethane or tri-chlor benzol. Acetone and alcohol do not dissolve rubber.

Hot Vulcanisation.—Without vulcanisation it is doubtful whether there would be a rubber industry worthy of the name. The hot process, discovered by Goodyear in 1839, depends essentially upon mixing raw rubber, as described later, with 8-10 per cent. of sulphur, or with Sb_2S_3 if it is not to be used for cut sheet, elastic threads, etc., with fillers, etc., and heating under pressure to 130°-140° C. for 2-3 hours. The rise of temperature should be slow, occupying from $\frac{1}{2}$-$\frac{3}{4}$ hour.

As a general rule the degree of vulcanisation is increased (*a*) by prolonging the time of cure; (*b*) by raising the temperature; and (*c*) by increasing the amount of vulcanising agent.

Hot vulcanisation yields best results when the goods are under high pressure, which is obtained either in presses or by wrapping tightly with fabric, *e.g.*, for curing hose and tyres. In the *open* or *steam cure* live steam is admitted into a kind of autoclave (Figs. 159 and 160), into which the goods, wrapped with canvas or in moulds, are placed; the vulcanising chamber is sometimes steam-jacketed. *Press-curing* is carried on between the steam-heated platens of hydraulic presses. This process has the advantage of high pressure, but the upper and lower platens being at different temperatures, the products are not uniform. In recent years the presses have been fitted with chambers into which the lower platens are raised, thus combining the advantages of the live steam and press cures. *Continuous processes.*—In order to enable great lengths of cable, hose, and proofed fabrics to be cured uniformly, they are passed at a regulatible speed through a steam-jacketed or otherwise heated chamber. The hot air process is applicable to other classes of goods, but is seldom used with proofed cloth.

Vulcanite, Ebonite, and Hard Rubber are produced by employing a considerable excess of sulphur, say 40 per cent., and by extending the vulcanising operation over 6 hours. Such hard sorts of rubber are used for making combs, handles, etc., and in the electrical industry as an insulating material. It should be unacted upon by acids and alkalies.

Cold Vulcanisation, discovered by Alexander Parkes in 1846, and applied more particularly to proofed cloth, is brought about by means of a 2-3 per cent. solution of sulphur chloride in CS_2. This process is not applicable to thick goods. The rubber mixing, which is conducted in the usual manner, as described later, but without the addition of sulphur, is rolled out into a sheet and dissolved in naphtha. The swollen dough, rendered homogeneous by being worked between rolls, is spread upon the cloth in the machine shown in Fig. 162. The fabric is placed on a roller, as shown at the right hand of the figure, then it is passed over the upper roller, above which is situated a doctor for adjusting the thickness of the layer, and in front of the doctor the dough. In its passage over the steam-heated table B, the fabric is freed from solvent. As a general rule a number of layers are applied. The fabric is now conveyed to another machine, upon which it is cured by unwinding it from one roller and winding it upon another, by allowing it in its passage to contact with a third roller dipping into the sulphur chloride bath.

Accelerators.—Some substances when introduced into rubber mixings considerably shorten the time required for vulcanisation, hence they are called accelerators.

The more important inorganic compounds are PbO, CaO, MgO, and Sb_2S_5, and soft resinous rubbers, which cannot be properly vulcanised when mixed with S alone, can be cured with the aid of these accelerators.

Esch and Seidl have shown that PbO stimulates the reaction between the S and the rubber resin, which is accompanied by the evolution of much heat.

Bayer & Co. have recently patented (English Patents, 11,530, 1913; 11615, 1913) a number of organic nitrogen compounds as accelerators, including piperidine, methyl piperidine, piperidyl-dithocarbamic-acid-piperidine, monopiperidylurea, tetramethylene-diamine, and pentamethylene-diamine, small quantities of which (½-1 per cent.) are introduced into the rubber mixing.

Theory of Vulcanisation—Hot.—Weber concluded from his experiments that direct addition results in the formation of compounds varying from $(C_{10}H_{16})_{10}S_2$ to $C_{10}H_{16}S_2$, but this is very doubtful. *Erdmann* (Liebig's *Annalen*, 1908, 362, p. 133) assumes the formation of thiozonides corresponding with the ozonides. *Hübener* (*J.S.C.I.*, 1910, p. 289) concludes that mono- and disulphides are formed. *Bysow* assumes that in the primary stage mere physical absorption occurs.

Cold.—The earlier experiments of Henriques and Weber led them to assume the formation of direct addition products, according to Weber varying from $(C_{10}H_{16})_{24}S_2Cl_2$ to $(C_{10}H_{16}S_2Cl_2)_{20}$. *Hinrichsen* assumes the formation of a body $(C_{10}H_{16})_3S_2Cl_2$, which forms a solid solution with the rubber, this solid solution containing varying quantities of absorbent "free sulphur." *Wo. Ostwald* has recently propounded a theory of both hot and cold vulcanisation to the effect that colloidal absorption occurs and not chemical reaction, but this seems to be disproved by the experiments of *Alexander*, who has shown that the tetrabromide and nitrosite derivatives obtained by precipitation from solutions of vulcanised rubber contain all the S of vulcanisation.

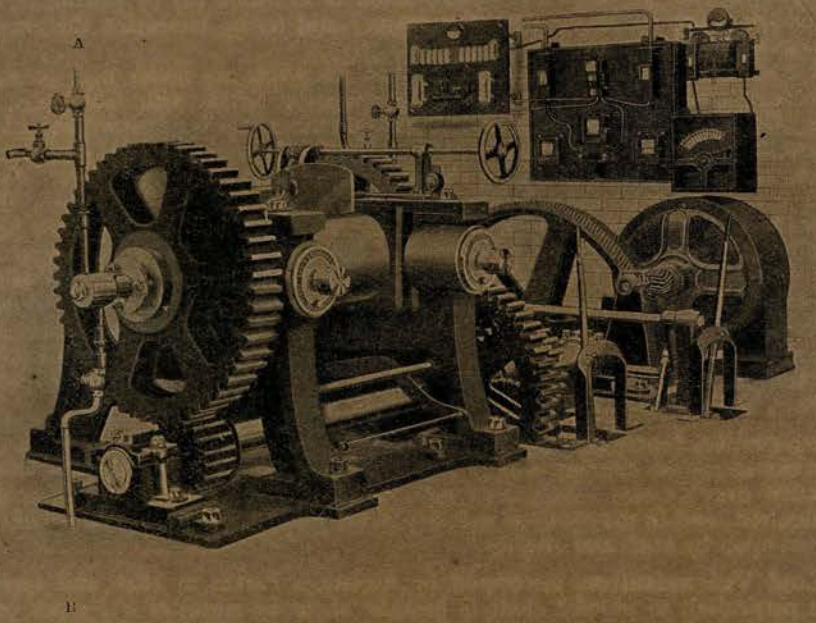


FIG. 161.—Grinder and Mixer. (David Bridge & Co., Castle on, Manchester.)

Manufacture of Rubber Goods.—*Mixing*—For certain classes of goods, such as cut sheet and elastic thread, sulphur is the only ingredient added, but in general other additions are made, sometimes to the extent of 75 per cent., viz., *fillers*, such as factis, or "oil substitute" (see under rubber substitutes), zinc oxide, chalk, rubber waste, etc.; *pigments*, such as "golden" sulphide (antimony sulphide),

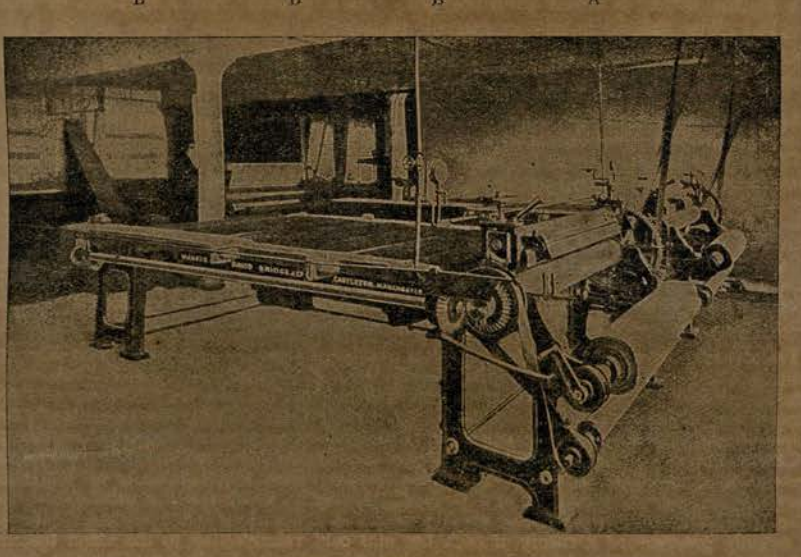


FIG. 162.—Spreading Machine (for garment cloth, card clothing, fine sheet, waterproofing, etc.).

lithophone, cinnabar, etc.; *for toughening*, balata, magnesia, iron oxide, kaolin, etc.; *for closing pores*, bituminous substances, etc. The mixing machine (Fig. 161), resembles the washer already described. The rolls are smooth and hollow for receiving steam or cold water supplied to trunnions through pipes, A, B, and are run at differential speeds. The raw rubber sheet which has been washed and dried in the factory as described above, is rendered plastic at about 50° C. by being passed a number of times (*masticating*) through the heated rolls of the mixer, gradually closing the "nip," the fillers, etc., are then sprinkled on a little at a time.

Calendering.—When a homogeneous sheet has been obtained it is usually taken direct to the calender (Fig. 163), the bowls of which must be truly turned, are very heavy and are also steam-heated. For the production of ordinary sheet

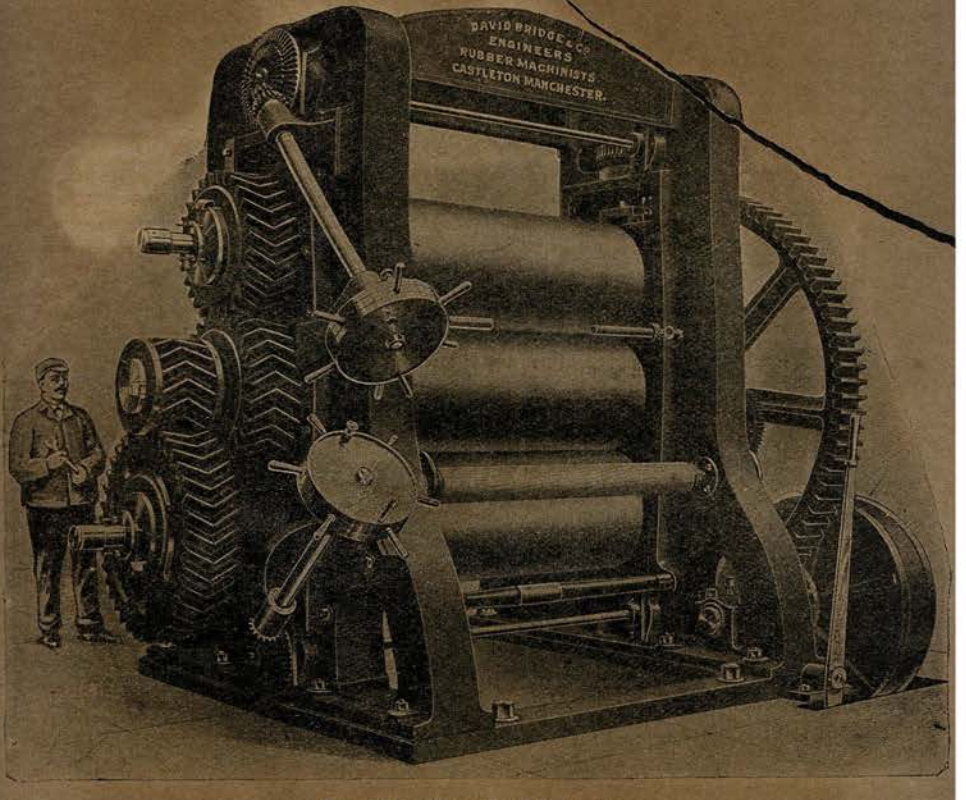


FIG. 163.—Three-Bowl Calender.

(1 mm.-1 cm. thick) the bowls run at even speed, and the dough is placed in the nip of the two upper bowls. The rotation of the bowls carries it round as a thin sheet to the lower nip, where it is transferred to a cloth which passes between the lower bowls and is wound upon a roller shown in front of Fig. 163, the cloth preventing adjacent layers from cohering. After an interval of rest the sheet is vulcanised. The process of building articles from calendered sheets is termed "*making up*," and requires great skill.

Cut sheet, which is gradually being displaced by calendered sheet, is employed for tobacco-pouches, etc. The washed and dried rubber is thoroughly masticated, pressed into blocks, frozen in refrigerating chambers, and cut into sheets.

Elastic thread is cut from calendered or spread sheet, rolled with a fabric

into a cylinder after dusting with French chalk, vulcanised, unrolled, coated with shellac solution, wound on a roller, and cut into thread.

Forcing or **Squirting** solid tyres, inner tubes of tyres, tubing, etc., is done in the extension press shown in Fig. 164. The warm rubber mixing is fed through a hopper fitted with an automatic roller-feed to a steam-jacketed Archimedean screw, rotated by the gear shown on the left, and is forced through the die shown on the right. This die is provided with a central spike for generating the hollow in tubes, or with a wire to serve as a core in solid tyres.

Tyre covers are usually made up by hand upon a mandrel from proofed

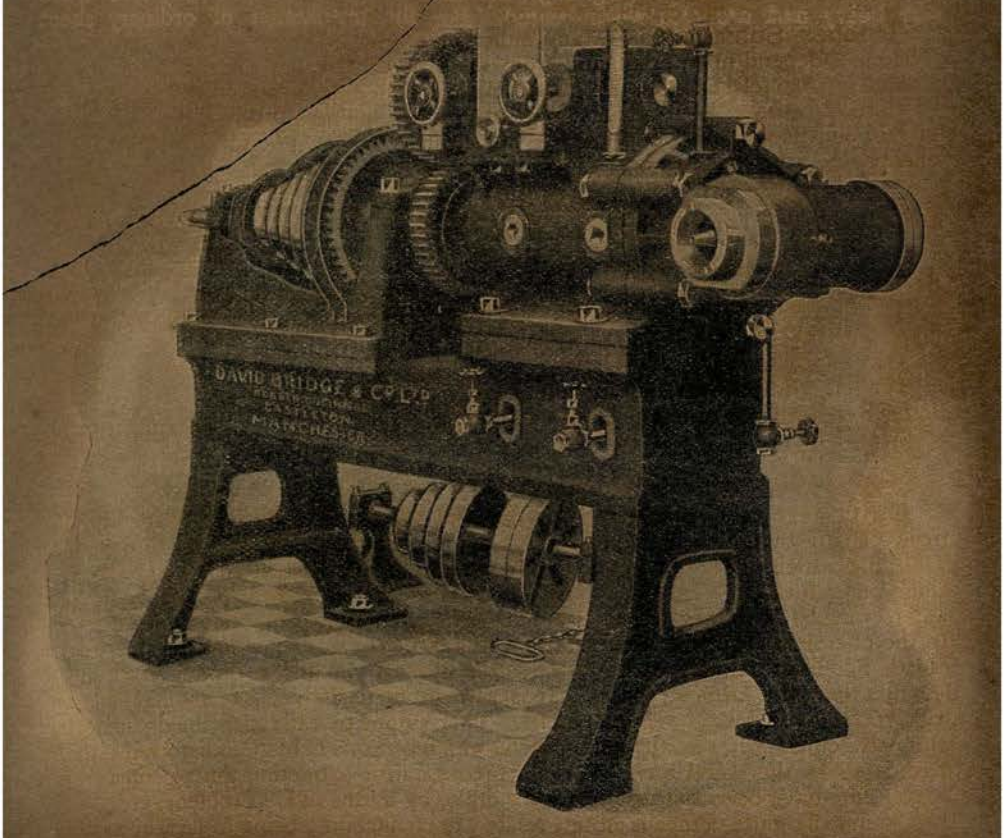


FIG. 164.—Forcing Machine (extrusion).

canvas and calendered sheet; *tyre-tubes* and other *tubing* by building up calendered sheet cut to the desired width; *hose* by building up the cheaper grades by lapping on a mandrel, and by other methods; direct moulding, stamping from calendered sheet, or cutting from cylinders are also used for some kinds of goods.

De-vulcanisation and Re-manufacture of Rubber

In the "reclaiming" of waste the fibre is usually removed by means of alkali or sulphuric acid, the S by treatment with alkalis, thiosulphate, etc. It has been claimed that some processes remove combined as well as free sulphur. Waste rubber has also been dissolved under pressure in benzine, etc., and utilised in the form of a solution. It is often ground up and used as a filler with raw rubber.

Of late years a new and valuable process, patented by Thomas Gare (Patent Specification, 12,454, A.D. 1906), and modified by Hyatt, Imnisch, and others, as described in later specifications, has been invented, by which it is claimed that old and worn rubber articles can be "reformed" and made as good as new without any addition. The process depends upon subjecting the rubber, preferably finely ground, to the action of high pressures, so as to exclude all air from the interstices, and then, whilst the rubber is still under pressure, subjecting it to temperatures above that of vulcanisation. In this process no attempt is made to remove the sulphur. The process depends upon the fact that, when air is excluded, rubber can be subjected to a high temperature, and can even be melted, without destroying its elasticity and compressibility, so long as it is allowed to cool without access of air.

Rubber Substitutes.—Many substitutes for rubber have been proposed. The chief depend upon producing from oils, more particularly drying oils, such as linseed oil, an elastic mass by "vulcanising" with S ("brown substitute"), S_2Cl_2 ("white substitute"), or Sb_2S_5 ("red substitute"). These products are known as oil rubber, factis, or white or red substitutes. They are chiefly valuable as cheapening additions for raw rubber.

Brown Factice is usually made by heating together rape oil and sulphur; **White Factice** by vulcanising castor oil with sulphur chloride, S_2Cl_2.

Mixtures of glue or gelatine, and glycerin, oils, or other softening agents, after treatment with tannic acid, chromates, or formaldehyde, have also been used as substitutes for rubber; for example, as cores for tyres and coverings for rollers. "Elastes" belongs to this class.

Cores and fillings for tyres have also been made by injecting into or generating in rubber, gelatine, etc., air or other gases. The inventions of the Pneumatic Tyres Syndicate are of this nature.

GUTTA-PERCHA

Gutta-percha is obtained from the *Isonandra gutta* (East Indies) and other trees, usually by felling the trees and "ringing" the bark at intervals of 12-18 in. The milk which oozes out in the better kinds soon coagulates, and is then boiled alone or with water. In order to clean the product it is reduced, softened in hot water, washed with hot water, strained, masticated between rollers, and sheeted. In the chemical cleansing process small pieces of raw gutta-percha are steeped in caustic alkali or chloride of lime, the latter process yielding a product containing less dirt than the former process. It is sometimes desirable, *e.g.*, in making golf balls, to remove resin from gutta-percha. This is done by extracting the dry material with petroleum spirit, etc., the gutta-percha which remains behind undissolved is then masticated in the usual way. Various processes for extracting gutta-percha from leaves, etc., have been suggested; for example, by means of CS_2, toluene, etc.

Chemically gutta-percha is closely related to caoutchouc, being in fact, according to Harries, a stereo-isomeride, of formula $(C_{10}H_{16})_n$, and, like caoutchouc, it forms an ozonide, $C_{10}H_{16}O_3$, which is decomposed by water into laevulinic aldehyde.

Physically, however, there is little resemblance; gutta-percha does not possess elasticity like caoutchouc; but when warmed is extremely plastic, and when pressed in forms gives the finest relief work in exact detail. Gutta-percha at ordinary temperatures is hard but not britttle; it is an excellent electric insulator, and is largely used in the manufacture of electric cables, especially marine ones, because, as compared with rubber, it possesses a greater power of resistance towards water under high pressures.

BALATA

Balata (from the "bullet" tree or *Sapota mulierii*) is midway in physical characteristics between indiarubber and gutta-percha, and is largely used for coating canvas for belting, and as a soling for shoes and boots. The milk is obtained by

removing the outer bark before tapping, and is coagulated by evaporation or by spirits of wine.

Statistics.—The accompanying figures give the growth of the world's production of crude rubber (caoutchouc): 1890, 29,330 tons; 1895, 34,827 tons; 1900, 52,864 tons; 1905, 68,879 tons; 1910, 76,553 tons; 1911, 88,000 tons; 1912, 98,950 tons; 1913, 112,000 tons.

The world's production of all grades of rubber in 1911 and the approximate price of these various grades of rubber on 11th May 1912 was as follows:—

	Output in Tons.	Price per lb.
		s. d. to s. d.
Amazonas and Brazil (para)	39,000	4 7 to 4 7½
Ceylon and Malaya (plantation)	14,200	4 11 „ 5 0
Africa and the rest of the world	34,800	2 1 „ 4 0
	88,000	

The production of **plantation rubber** was:—1912, 28,500 tons; 1913, 470,000 tons.

It is estimated that the total raw rubber output in 1915-1916 will be nearly 150,000 tons. At present the United States consume one-half the world's output, the United Kingdom and Germany each one-sixth.

Brazil, *Bolivia*, and *Peru* exported 39,500 tons in 1911, against 40,000 in 1910; in 1912 the export was 43,000 tons, and in 1913, 39,700 tons; *Mexico* in 1911 exported 9,200 tons of guayule; *Ceylon* and *India* 2,750 tons in 1911; *Malaya* 11,400 tons in 1911; *West African Coast* 15,000 tons in 1911. The exports from the *Straits Settlements*, *F.M.S.*, and *Ceylon* for 1913 was 71,000,000 lbs., value £11,000,000.

The quantity of caoutchouc imported into England was 30,000 tons in 1906 (value £10,000,000), and 43,800 tons in 1910 (value £26,000,000). The value of the manufactured rubber goods imported into England in 1910 was £627,000, and of the exported was £1,800,000, while the exported **rubber waste** was £356,000. The price of the best Para rubber in 1911 was 6s. per lb. In 1910 it once rose to 13s. a lb. It will probably fall to 2s. per lb. or under in a few years.

The import of **gutta-percha** into the United Kingdom was—1906, 53,000 cwt. (value £489,000); 1910, 97,000 cwt. (value £1,136,000).

It is stated that between 1900-1910 no less than £70,000,000 was expended on rubber plantations. 850,000 acres are under cultivation in the East (1911), and 80 acres in Mexico, Nicaragua, etc.

Estimated yield per tree (Hevea), age 5 years, ½-¾ lb.; 7 years, 1¼-1½ lbs.; 12 years, 3 4 lbs. Some 15-30-year-old trees have yielded 15 to 20 lbs. per tree per year.

Tappings per year—Hevea, 150-160; Castilloa, 4-5. Brazil, Peru, and Bolivia produce about one-half the world's rubber.

THE ANALYSIS OF RUBBERS

By GERALD HARGRAVE MARTIN, F.C.S.,
Rubber Chemist

LITERATURE

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Raw rubbers contain—1. Dirt, sand, bark; 2. moisture; 3. carbohydrates (sugars of the inosite class); 4. resins; 5. nitrogenous substances (proteins, enzymes); 6. rubber hydrocarbon (caoutchouc); 7. ash.

The loss on washing is determined by allowing a stream of water to play on the rubber while it is repeatedly passed through the washing rolls.

By this means the dirt, sand, pieces of bark, etc., are squeezed out of the rubber and carried away by the water, which also dissolves out most of the sugars.

Plantation rubbers are washed before exportation, and for wild rubbers the loss on washing is determined on a large sample in the factory, so the rubber chemist commences his analysis on a sample of the washed and dried rubber.

As acids are used for coagulating the latex on many plantations, and free acid has an injurious effect on rubber, the sample should first be tested for acidity.

Moisture may be estimated by placing the rubber in vacuum over sulphuric acid for several days, until the weight is constant, but is more conveniently estimated during the extraction with acetone.

To estimate the resins, 2-5 gr. of the rubber are cut into small cubes, or better, the rubber is rolled into a very thin sheet, which is extracted with acetone for six hours in a Soxhlett extractor. Of low grade highly resinous rubbers such as Jelutong, Guayule, etc., 1-2 gr. will be enough.

The acetone extract is brought into a tared flask, the acetone is distilled off in a water bath, and the residue dried in the steam oven for one hour, and then the heating is continued for periods of 15 minutes until the weight is constant. (The drying may be hastened by placing the flask on its side in the steam oven, so that the heavy vapours pour out, and the heating should not be unduly prolonged, as the resins absorb oxygen, so that the weight increases.)

Sometimes a white crystalline ring is observed on the sides of the flask; this is said to consist of sugars which escaped solution during the washing.

The acetone extracted rubber is placed on a watch glass, and dried in the steam oven, or better, in a vacuum oven.

If dried in the air, the rubber should be heated for one hour, and then for periods of 15 minutes, until the weight is constant, or begins to increase. (Acetone extracted rubbers absorb oxygen rather rapidly.)

The difference between the weight lost by the rubber and that of the acetone extract represents the weight of the moisture contained in the rubber.

The insoluble matter is determined by dissolving 1 gr. of the rubber in $CHCl_3$ or C_6H_6 (1-3 days), and the insoluble matter is separated by filtering through a Gooch crucible fitted with asbestos or glass wool, or better, by centrifuging.

The residue is washed first with the solvent used, then with naptha, and finally with petroleum spirit, after which it is dried, weighed, and then ashed. The difference between the weights of the insoluble residue and its ash represents the weight of insoluble organic matter.

Schidrowitz estimates the total insoluble matter by placing ½-1 gr. of the rubber in a 200 c.c. stoppered measuring cylinder, which is then filled to the mark with C_6H_6, and allowed to stand with occasional shaking till solution is complete (2-3 days).

An aliquot portion (20-50 c.c.) of the clear liquid is then pipetted off from the upper portion of the cylinder, and placed in a tared flask. The benzene is evaporated on the water bath, and the residue dried and weighed.

If 50 c.c. were removed, the difference between the weight of rubber taken and four times the weight of the residue from the 50 c.c. of solution gives the amount of insoluble matter in the rubber.

Nitrogen in rubbers is determined by Kjeldahl's method. 1-2 gr. of the rubber are heated on a sand bath with 12 c.c. of conc. H_2SO_4, 8 c.c. of fuming sulphuric acid.

After the acid has been boiling for an hour, 8 gr. of dry K_2SO_4 are added, and the heating is continued until a clear, colourless, or pale yellow melt is obtained, or the rubber may be boiled in the sulphuric acid mixture for 3-4 hours; and then a little $KMnO_4$ is added cautiously, a few crystals at a time, to the hot acid, and the heating continued until a clear pale yellow liquid is obtained. (Many rubbers contain a little iron, which causes the pale yellow colour.)

The product is then cooled, diluted with 200 c.c. of water, again cooled; 80 c.c. of NaOH solution S.G. 1.3-1.4 added, a piece of zinc dropped into the distillation flask, and 100 c.c. of the liquid distilled into 100 c.c. of $\frac{N}{10}H_2SO_4$, with the usual precautions.

The excess of $\frac{N}{10}$ H_2SO_4 is titrated with $\frac{N}{10}Ba(OH)_2$, or Na_2CO_3, using methyl orange as an indicator. The nitrogen figure, when multiplied by 6.25, is usually regarded as representing the amount of proteid in the case of washed rubbers.

To determine the ash, about 2 gr. of the rubber are placed in a porcelain crucible (preferably glazed on the inside only), which fits in a circular hole in a piece of asbestos board.

The crucible is heated with a very small Bunsen flame until fumes are no longer evolved, and the carbon deposited on the sides of the crucible is burnt off at the mouth of a muffle furnace, or over a large Bunsen flame. Hevea rubbers (Para, Mollendo, Plantation Para, etc.), may only contain 0.2 per cent. of ash, so in this case about 10 gr. of the rubber should be taken and fumed off, 2 or 3 gr. at a time.

The ash may contain silica, lime, alumina, magnesia, iron oxide, sulphates, phosphates, and chlorine, which are determined by the ordinary methods of analysis. Several methods have been proposed for *the direct estimation of the rubber hydrocarbon*, but this is best determined by difference. The percentage values found for moisture, acetone extract, insoluble organic matter, and ash, when added together and subtracted from 100, give the per cent. of caoutchouc contained in the rubber.

Vulcanised Rubbers.—Owing to the very large number of both organic and inorganic substances which are introduced into rubber mixings, an exact separation of all the constituents is often very difficult and sometimes impossible.

The following scheme of separation, which is based on the work of Henriques and Weber, is the best which has yet been devised, and may be used for both soft rubbers and vulcanites. The rubber (about 2 gr.) is extracted with acetone for ten hours; this dissolves out rubber resins, free S, and any oils or solid hydrocarbons which the rubber may contain.

The rubber is next extracted with pyridine for one hour, which separates any tar, pitch, or bituminous substances, and the sulphur combined with them.

These substances, which need only be sought in dark rubbers, may be detected by warming a piece of the rubber with C_6H_6, or $CHCl_3$, when their presence is revealed by the formation of a dark-coloured and usually fluorescent solution. If they are absent, the pyridine extraction may be omitted.

The rubber is then boiled with 50 c.c. of a 5 per cent. alcoholic solution of NaOH for four hours with alcohol in a Soxhlett extractor, and then with water. This removes the factice (rubber substitutes), blown and polymerised oils, with the sulphur and chlorine contained in the factice.

The rubber is then heated in a flask with 60 gr. of a nitronaphthalene for one hour to 180°, cooled, and 150 c.c. of benzene are added.

The liquid is allowed to stand until the insoluble matter settles out, when it is filtered, and the residue washed with benzene, dried, and weighed. In this way the caoutchouc and the sulphur and chlorine combined with it are removed from the mixing. The residue is then extracted with boiling water to remove any starch or dextrine.

The residue may now contain mineral matter, free carbon, fibrous minerals, and sulphur in inorganic compounds.

The free sulphur in the acetone extract may be estimated by heating the extract with fuming nitric acid, evaporating the solution to a thin syrup, which is transferred to an evaporating dish and concentrated on the water bath to a thick syrup, 2 gr. of fusion mixture are added, and the mixture well stirred.

The basin is cautiously heated until the mixture has become white, when it is strongly ignited.

The residue is dissolved in hot water, the solution filtered, the filtrate acidified with HCl, and boiled, and the sulphate precipitated with barum chloride.

As a small loss of sulphur is liable to occur during the oxidation with nitric acid, a better method is to boil the acetone extract with 20 c.c. of alcohol, and 0.6 gr. of NaCN for two hours.

The alcohol is distilled off, the residue is taken up in 100 c.c. of water, 5 c.c. of a saturated solution of iron alum is added, and the liquid heated to 95 with constant stirring, and filtered. 5 c.c. of concentrated HNO_3 are added to the cooled filtrate, which is then made up to 500 c.c.

The blood-red solution of ferric thiocyanate is titrated with $\frac{N}{10}$ $AgNO_3$ (1 gr. Ag = 0.297 gr. of S).

Mineral oils usually reveal their presence by imparting a fluorescence to the acetone extract. If waxes are present, the residue from the acetone extract is warmed with 50 c.c. of 96 per cent. alcohol, filtered, and the residue washed with 25 c.c. of alcohol. The filtrate is then cooled to −4°, the wax is filtered and washed with 100 c.c. of 96 per cent. alcohol cooled to −4°.

The figures obtained by weighing the residue left after distilling off the pyridine from the pyridine extract are of doubtful value, as pyridine dissolves some of the rubber, while bitumen is not entirely soluble in pyridine. The sulphur may be estimated by oxidation with HNO_3, and fusion mixture as described for the acetone extract.

The alcoholic soda extract should be tested for mineral fillers, some of which, such as antimony, sulphide, and zinc oxide, are partially extracted.

The total sulphur may be de ermined by mixing 0.2 gr. of the finely divided rubber or ebonite with 6-7 gr. of Na_2O_2, and 0.1 gr. of powdered sugar in a nickle crucible, and covering the mixture with a thin layer of Na_2O_2.

The crucible is placed in a basin containing a little water, and the mixture is fired by passing a red hot wire through a hole in the crucible lid. The residue is dissolved in the water in the dish, nearly neutralised with HCl, boiled and filtered to remove a few smuts which are formed (the liquid should not be black), acidified with HCl, boiled and precipitated with $BaCl_2$ as usual.

As Na_2O_2 usually contains traces of S, a blank test must be made with the sample used.

By another method the finely divided rubber is heated with a mixture of ZnO and KNO_3 over a spirit Bunsen (to avoid SO_2) gently until the vigorous action is over, and then to a red heat. The product is boiled with HCl, filtered, and precipitated with $BaCl_2$ as usual.

Cold vulcanised rubbers and white factice (which appears in the alcoholic soda extract) contain **chlorine**, which may be estimated by precipitating as AgCl in the usual manner after the organic matter has been destroyed by ignition with fusion mixture.

The mineral fillers are determined by the usual methods of inorganic analysis, and with the exception of Pb, Sb and Hg may be estimated in the ash.

Pb can only occur in black rubbers, and Sb_2S_3 is usually put into red rubber mixings, while some special red rubbers owe their colour to vermillion (HgS).

These three metals, which are never introduced together into a rubber mixing, are determined after the organic matter has been destroyed by heating the rubber with nitric acid and ammonium presulphate.

Pb may be estimated by making the liquid alkaline with NH_4OH, digesting with ammonium acetate, filtering from any insoluble matter (SiO_2, $BaSO_4$), acidifying with CH_3CO_2H, and precipitating as $PbCrO_4$.

Hg and Sb are estimated by adding HCl to the liquid, diluting and passing SH_2 gas.

The HgS may be freed from S by extraction with ammonium sulphide, and the Sb is best converted into Sb_2O_4 by evaporation first with dilute HNO_3, then with conc., and finally with fuming nitric acid, when it is ignited and weighed.

The organic constituents of rubbers may also be destroyed by Gasparini's electrolytic method, in which Hg of the rubber is placed in contact with Pb electrodes, in 15-20 c.c. of fuming nitric acid, in a special apparatus (Gasparini, *Gazz. Chim. Ital.*, 37, p. 426).

A continuous current (10 amperes and 8-16 volts) is passed until all organic matter is oxidised (two-seven hours).

This method is said to give good results for the estimation of total sulphur, chlorine, mercury, etc.

MECHANICAL TESTS.

These chemical tests should be supplemented by **Mechanical Tests**, *e.g.*, for elasticity, breaking strength, etc., for which special machines are employed.

It is interesting to note that viscosity measurement is a more accurate test of the strength of rubber than "hand-pulling" or mechanical tensile tests. Schridowitz and Goldsbrough (*Journ. Soc. Chem. Ind.*, 1909, p. 3) used filtered dilute solutions in an Ostwald double-bulb viscometer with pure benzene as solvent, and a temperature of 20° C. Comparative determinations only are necessary, the viscosity of pure benzene being taken as 1. They showed that a straight line law is obeyed for dense solutions between the viscosity and concentration, and thus by assuming a concentration of 100 per cent. they were able to obtain values for solid matter. These observers conclude that within the same species viscosity measurements vary directly with strength and "vulcanising capacity," and that even when comparing species with species high viscosity indicates strength.

The capacity for vulcanisation should also be investigated by using a range of methods (open cure, press cure, etc.), of time, temperature, and different mixings.

The usefulness of a sample for particular purposes may be ascertained by mechanical tests on best-cure rubber, such as breaking-strain, elongation at break, nature of hysteresis curves, and elongation of curves, etc., compression under given load, recovery after compression for fixed time, elasticity (by dropping a steel ball on a sheet of the sample and comparing heights of drop and rebound), abrasion and hardness tests, specific gravity, di-electric strength, effect of reagents on weight, volume, tensile properties, etc., dry heat (132° C. for 1 hour), and moist heat (steam, 160° C. for 3 hours) tests, porosity.

II.—SYNTHETIC RUBBER

By G. Martin, Ph.D., M.Sc.

LITERATURE

The following are important papers:—

W. H. Perkin, Jun.—"Butadiene, Isoprene, and their Homologues." *Journ. Soc. Chem. Ind.* (1912), 616.

C. Harries.—*Liebig's Annalen* (1911), **383**, 157-227 (Abstract in *Journ. Soc. Chem. Ind.* (1911), 1073); *Gummizeit.* (1910), 850; (1907), 21, 823; (1906), 1277; *Zeits. Angew. Chem.*, **19**, 1330. "Ber." (1904), **37**, 2708; (1905), **38**, 1195, 1198, 3985, 3989.

Tilden.—*Chem. News*, **46**, 120 (1882); **65**, 265 (1892); *Journ. Chem. Soc.*, **45**, 411 (1884), Brit. Assoc., 1906.

G. Bouchardat.—*Bull. Soc. Chim.*, **24**, 108; *Comptes Rend.*, **80**, 1446 (1875); **89**, 361, 1117 (1879).

Kondakow.—*Journ. Pr. Ch.* (2), **59**, 299 (1889); **62**, 175 (1900); **63**, 113 (1901); **64**, 109-110 (1901); *Revue générale de Chimie*, 1912.

Willstatter.—"Ber.," **38**, 1975; **40**, 957, 3994.

A. Klages.—"Kautschuk u. Kautschukersatzstoffe," *Z. Angew. Ch.*, **34**, 1505 (1911).

The following are the numbers of the more important patents bearing on the manufacture of synthetic rubber:—

English Patents.—21,772, 1907; 13,252, 1908; 15,299, 29,277, 29,566, 1909.
English Patents of 1910.—4,001, 4,189, 4,572, 4,620, 5,931, 5,932, 8,100, 9,219, 14,040, 14,041, 15,254, 17,734, 24,790, 25,850.
English Patents of 1911.—1,124, 1,125, 6,540, 9,721, 9,722, 15,203, 15,204, 16,925, 18,935, 27,361.
French Patents of 1911.—434,586, 433,825, 433,322.
English Patents of 1912.—227, 448, 3,873, 5,555, 12,770, 12,771, 12,772, 12,773, 13,051.
French Patent of 1912.—438,789.

The term "synthetic rubber" is used as distinct from the term "rubber substitutes" to indicate products which are claimed to have the same or approximately the same chemical constitution as caoutchouc or the prime constituent of caoutchouc, and not merely bodies having similar physical properties to caoutchouc or india-rubber.

When certain unsaturated hydrocarbons containing the grouping :C:C.C:C: are allowed to polymerise, they form a series of caoutchoucs which possess many of the properties of the best sorts of natural caoutchouc, including the power of vulcanising.

The hydrocarbons from which technical synthetic rubber has been formed are:—

Butadiene (Erythrene, Divinyl), $CH_2=CH-CH=CH_2$.

β-Methyl Butadiene (Isoprene, Methyl Divinyl), $CH_2=C(CH_3)-CH=CH_2$.

β-γ-Dimethyl Butadiene (Di-isopropylene, dipropylene), $CH_2=C(CH_3)-C(CH_3)=CH_2$.

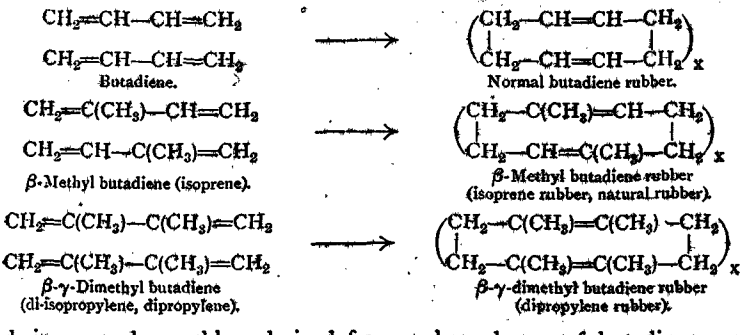
Butadiene is at ordinary temperatures a gas.

Properties of Isoprene (Methyl Vinyl, β-methyl butadiene).—Colourless liquid with penetrating smell; B.P., 36°-37° C.; density, 0.6804; mol. refract., MR_D (21°)=25.45; mol. disp., $MD_{\gamma-\alpha}$ (21°)=1.25.

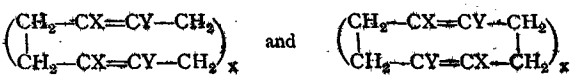
Properties of β-γ-Dimethylbutadiene.—Colourless liquid; B.P., 71° C., n_D = 1.43751; mol. refract., 29·65; density (20°), 0.7272; $M_\gamma-M_\alpha$=1,41.

The higher homologues of butadiene also produce rubbers; *e.g.*, β-methyl-γ-phenyl butadiene (phenyl isoprene), $CH_2=C(CH_3)-C(C_6H_5)=CH_2$, has been shown by A. Klages and E. Lauk ("Dissert.," Heidelberg, 1904) to polymerise to a rubber-like body which vulcanised to a product inferior to ebonite. Doubtless further research will bring to light technically important higher rubber.

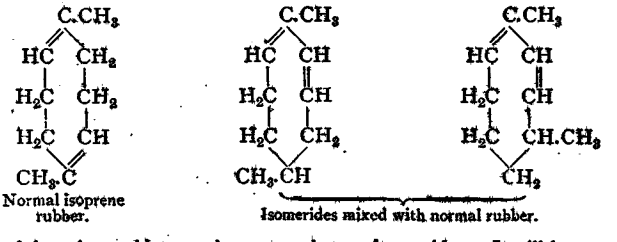
The polymerisation may be regarded as taking place thus:—



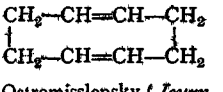
And, in general, a rubber derived from a homologue of butadiene, such as $CH_2=CX-CY=CH_2$, would produce rubbers of the formulæ:—



As a matter of fact the polymerisation is a much more complex matter than this. Thus sticky or liquid lower polymerides are first formed, and the final polymerisation product is formed gradually by further condensation. Moreover, if the polymerisation proceeds too far and the molecules become too condensed, hard brittle products may be formed. Also Harries has shown (*Annalen*, 383, 157-229) that different rubbers are obtained by using different polymerisation agents, *e.g.*, when butadiene is polymerised by heating alone or with acetic anhydride, it yields a "normal butadiene rubber," $(C_8H_{12})_x$, while when polymerisation is effected by sodium wire it yields quite a different rubber, called "sodium butadiene rubber." In a similar manner several isomeric rubbers are obtained by polymerising isoprene and dimethyl butadiene respectively. Thus, for isoprene rubber (natural rubber) Harries suggests (*Annalen*, 383, p. 187) the presence of three isomerides, which have the double linkage in a different position, thus:—



Moreover each of these isomerides may have several stereoisomerides. It will be seen that according to Harries' views the basis of rubber is the hydrocarbon cyclopentadiene (1:5) which contains a ring of eight carbon atoms:—



Pickles (*Journ. Chem. Soc.*, 1910) and Ostromisslensky (*Journ. Russ. Phys. Chem. Soc.*, 1912, 44, 204-244) suggest rings containing more than eight carbon atoms.

Identification of Rubbers.—Harries has shown that the only way to identify a rubber is to ozonise it, and then decompose the ozonide produced (see p. 358), because simple bodies are thus obtained which yield with phenylhydrazine finely crystalline compounds with sharp melting points, and so can be easily identified, and at the same time give an insight into the structure of the molecule. Although rubbers yield **bromides** and **nitrosites** (p. 359) yet these compounds are amorphous without sharp melting points, and so do not afford good means of identifying the various rubbers.

MANUFACTURE OF BUTADIENE, METHYL BUTADIENE (ISOPRENE), AND DIMETHYL BUTADIENE FOR THE PURPOSE OF MAKING SYNTHETIC RUBBER

Since rubber can be produced quantitatively from butadiene and isoprene, the problem of successfully producing synthetic rubber commercially resolves itself firstly into the manufacture of butadiene, isoprene, or dimethylbutadiene, as cheaply as possible, and secondly, into the polymerisation of these substances to rubber.

Manufacture of Butadiene (Erythrene, Divinyl)

1. **From Butyl Alcohol** (Fernbach's Fusel Oil).—Perkin (*Journ. Soc. Chem. Ind.*, 1912, **31**, 622) converts the butyl alcohol, $CH_3.CH_2CH_2CH_2OH$, into butyl chloride, $CH_3CH_2CH_2CH_2Cl$, by passing dry HCl gas into the heated alcohol, and then chlorinates the butyl chloride so as to produce dichlorides.

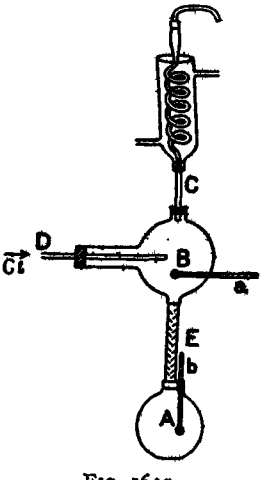


FIG. 164*a*.
Pim's Chlorinating Apparatus.

The difficulty that a large proportion of higher chlorides are produced by chlorinating under ordinary circumstances is got over by employing a special apparatus devised by Mr C. A. Pim.

The liquid is boiled in the vessel A (Fig. 164*a*) until the chlorinating chamber B is full of vapour and the liquid drops from the end of the reflux condenser C. Then a stream of dry chlorine is passed in through D, keeping, however, the butyl chloride in excess. During the chlorination process the apparatus must stand in a good light, and on dull days the ultra-violet light of a mercury lamp is used to facilitate chlorination. As fast as the higher-boiling dichloride is produced in B it drops back into the vessel A; and as this is provided with an efficient fractionating column E, only the lower-boiling butyl chloride can pass up into the chlorinating chamber B; the dichlorides are thus removed from the sphere of action of the chlorine and thus escape further chlorination. The liquid in A is finally fractionated and the dichlorides separated. *a* and *b* are regulating thermometers.

There are thus produced the dichlorides
1 : $2CH_3CH_2CHCl.CH_2Cl$ (B.P. 125),
1 : $3CH_3.CHCl.CH_2.CH_2Cl$ (B.P. 137), and
1 : $4CH_2Cl.CH_2CH_2.CH_2Cl$. These dichlorides are then passed over hot soda lime at a temperature of 470° C., whereby hydrochloric acid is abstracted and butadiene formed, thus :—

$$CH_3.CHCl.CH_2.CH_2Cl \xrightarrow[-HCl]{\text{Soda lime}} \underset{\text{Butadiene.}}{CH_2{=}CH{-}CH{=}CH_2}$$

Harries (*Annalen*, 1911, **383**, 181) also uses butyl alcohol and produces the bromide $CH_3CHBrCH_2CH_2Br$, which he also passes over heated soda lime.

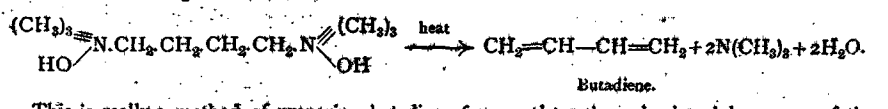
The commercial success of this method depends upon the production of cheap butyl alcohol. This is obtained by fermenting starchy mashes with **Fernbach's Cultures**, whereby a large yield of fusel oil containing no less than 65 per cent. of butyl alcohol is obtained (see pp. 314, 333).

2. **Butadiene from Aldehyde.**—Perkin (*loc. cit.*) also proposes to obtain butadiene from aldehyde (which is prepared from alcohol, and thus from starch) by treating it with very dilute potassium carbonate whereby aldol, $CH_3CH(OH)CH_2CHO$, is produced. This is reduced and yields 1 : 3-butylene glycol, $CH_3CH(OH)CH_2CH_2OH$; this is then converted into 1 : 3-dichlorobutane, $CH_3CHCl.CH_2CH_2Cl$, by dry HCl gas; and finally butadiene obtained by passing this over hot soda lime as above described.

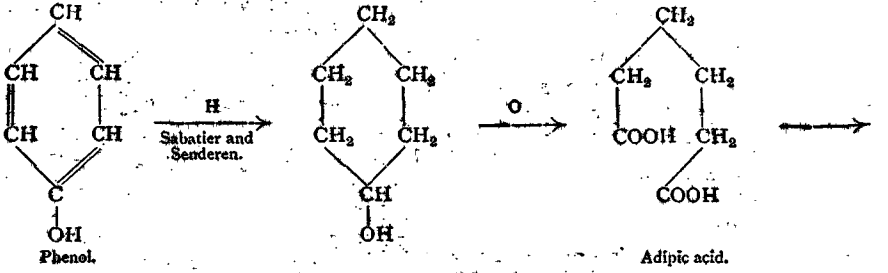
Here the starting point is starch, in the form of potatoes or grain, which are fermented to alcohol, which is then oxidised to aldehyde.

3. **Butadiene from Light Petroleum.**—*Fr. Bayer & Co., Elberfeld,* English Patent, 448, 1912, produce butadiene from cyclohexane and its homologues (derived from light petroleum) by passing the vapours over hot contact surfaces, especially over a spiral of aluminium silicate heated electrically to a dull red heat. The unchanged hydrocarbon is returned to the boiler, whilst the gases are freed by cooling from liquid hydrocarbons and the butadiene extracted from them. In their French Patent, 437,387, 1911, they decompose petroleum or its fractions or residues by means of hot contact surfaces, *e.g.*, a fraction of B.P. 70°-100° C., obtained from Caucasian petroleum, is passed in a state of vapour over a coil of platinum heated electrically to dull redness. The unaltered petroleum is returned to the container, whilst the gases are freed from low boiling hydrocarbons by cooling, and the butadiene is isolated either by strong compression and cooling and fractionating, or by a chemical process such as converting it into its tetrabromide. *Perkin and Weizman* (English Patent, 9,722, 1911) pass 1 : 2-butylene, $CH_3.CH_2.CH:CH_2$ (obtained by cracking petroleum), over heated finely-divided copper, whereby a mixture of butadiene, $CH_2:CH.CH:CH_2$ (by removal of H), and unchanged butylene results. The butadiene is then polymerised, and the unchanged butylene distilled off from the resulting caoutchouc.

4. **Butadiene from Phenol.**—Fr. Bayer & Co. (English Patents, 8,100, 1910; 18,935, 1911) produce butadiene by treating tetramethylenediamine, $NH_2CH_2CH_2CH_2CH_2NH_2$, with water and KOH, then adding methyl iodide, CH_3I, in small portions, when we get formed tetramethylenehexamethyl diamine iodide, $(CH_3)_3IN—CH_2—CH_2—CH_2—CH_2N(CH_3)_3I$. This is converted into the hydroxide $(CH_3)_3(OH)N—(CH_2)_4—N(CH_3)_3(OH)$ by silver oxide. When this is warmed it decomposes into butadiene, thus:—



This is really a method of preparing butadiene from coal-tar through phenol by means of the following series of reactions:—



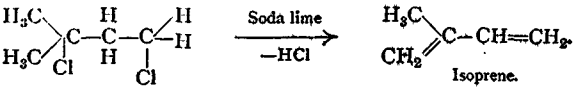
5. **Butadiene from Acetylene.**—Heinemann (English Patent, 20,772, 1908) produces butadiene by heating acetylene and ethylene together in a tube heated to dull redness, thus:—

$$\underset{\text{Acetylene.}}{CH{\equiv}CH} + \underset{\text{Ethylene.}}{CH_2{=}CH_2} \longrightarrow \underset{\text{Butadiene.}}{CH_2{=}CH{-}CH{=}CH_2}$$

Manufacture of β-Methyl Butadiene (Isoprene, Methyl Divinyl), $CH_2=C(CH_3)-CH=CH_2$

1. **Isoprene from Amyl Alcohol (Fusel Oil).**—W. H. Perkin (*Journ. Soc. Chem. Ind.*, 1912, 621) proposes to produce isoprene from **isoamyl alcoho**

$(CH_3)_2CH.CH_2.CH_2OH$, derived from commercial fusel oil, by converting it into the chloride $(CH_3)_2CH.CH_2CH_2Cl$, and then chlorinating this isoamyl chloride in a Pim's apparatus (p. 366*b*), so as to produce dichlorides, viz., isopropylethylene dichloride, $(CH_3)_2CH.CHCl.CH_2Cl$ (B.P. 142° C.); *gem*-dimethyltrimethylene dichloride, $(CH_3)CCl.CH_2.CH_2Cl$ (B.P. 152°-155°); and β-methyltetramethylene dichloride, $CH_2Cl.CH(CH_3).CH_2.CH_2Cl$ (B.P. 170°-172°). These dichlorides when passed over hot soda lime (at 470° C.) produce isoprene, the soda lime extracting the elements of hydrochloric acid, thus:—



The isoprene coming over is condensed by a freezing mixture and purified by fractionation.

Since amyl alcohol is derived from starch, this is a method of obtaining isoprene from starch.

2. **Isoprene from Light Petroleum.**—Isoprene has been produced from light petroleum or oil gas by isolating isopentane by distillation, converting it into dichlorides by halogenating, and passing the resulting dichlorides over hot lime, which removes the elements of hydrochloric acid and produces isoprene.

For example, C. Harries (German Patents, 243,075, 1910, and 243,076, 1910) passes the dihalogenides, $C_5H_{10}(Hal)_2$, or the monochlorhydrines, $C_5H_{10}(OH)(Hal)$, over soda lime or magnesium oxide heated to 600° C., whereby isoprene is produced in yields varying from 30 to 60 per cent. of the theoretical. The following substances were used:—

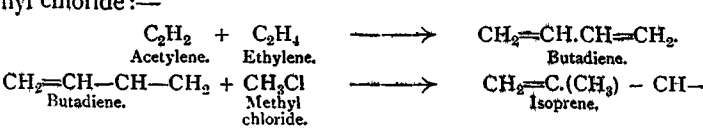
$(CH_3)_2CCl.CHCl.CH_3$, $(CH_2)_2CBr.CHBr.CH_3$, $(CH_3)_2C(OH).CHCl.CH_3$, and $(CH_3)_2.C(OH).CHBr.CH_3$,

and better yields were obtained with the bromides than with the chlorides.

The Badische Anilin-u. Soda-Fabrik (French Patent, 435,312, 1911) convert isopentane derived from petroleum or oil gas into monohalogen derivatives by submitting a mixture of Cl and an excess of isopentane to the influence of a mercury vapour lamp. The chloroisopentanes are then treated with hot lime, which removes HCl and forms trimethylethylene, $(CH_3)_2C=CH_2.CH_3$. This is converted into the dichloride $(CH_3)_2.CCl.CCl.CH_2CH_3$, and pure isoprene is prepared from this by passing it under reduced pressure over a catalytic agent such as alumina or $BaCl_2$ heated to 350° C.

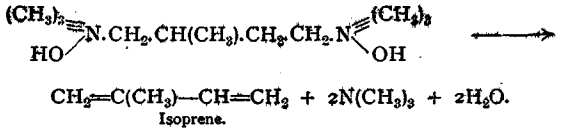
3. **Isoprene from Turpentine Oils.**—*Tilden* in 1884 (*Journ. Soc. Chem.*, **45**, 411) showed that isoprene can be obtained by passing **turpentine oil** through an iron tube heated to a dull red heat, but the yield was only 6 per cent. *Silberrad* (English Patent, 4,001, 1910) finds that the yield is greatly increased if the turpentine vapour is produced in a highly rarefied condition. *Heinemann* (English Patent, 14,040, 1910) obtains isoprene by passing the vapours of turpentine oil over heated, finely divided copper or silver at 450°-480° C. *Harries* (*Lieb. Ann.*, 1911, 383, 228) showed that good results are obtained by passing the vapours of turpentine oils over an electrically heated wire, the isoprene escaping, on account of its great volatility, through the top of a reflux condenser, while the heavier boiling turpentine oils are returned to the flask below. Fr. Bayer & Co., Elberfeld (French Patent, 438,789, 1911), pass nopinene (B.P. 165°-166°) over electrically heated surfaces and obtain a 20 per cent. yield of isoprene.

4. **Isoprene from Acetylene.**—Heinemann (English Patent, 21,772, 1907) produces isoprene first by combining acetylene and ethylene to form butadiene (divinyl) by passing the mixed gases through a tube heated to dull redness; the resulting butadiene is next converted into the methyl derivative by heating with methyl chloride:—



5. **Isoprene from Para-Cresol** (Coal Tar Product).—Fr. Bayer & Co., Elberfeld (English Patent, 8,100, 1910; 18,935, 1911) produce isoprene by heating tetramethyltetramethylenediamine, $NH_2.CH_2CH(CH_3).CH_2.CH_2.NH_2$, with KOH,

water, methyl alcohol, and methyl chloride, CH_3Cl, in an autoclave for twelve hours at 100° C., whereby the compound $Cl(CH_3)_3N.CH_2.CH(CH_3).CH_2CH_2.N(CH_3)_3Cl$ is produced. This is converted into the base by replacing the Cl with OH by treating with silver oxide in the usual manner. The base, when distilled, breaks up into isoprene, thus :—

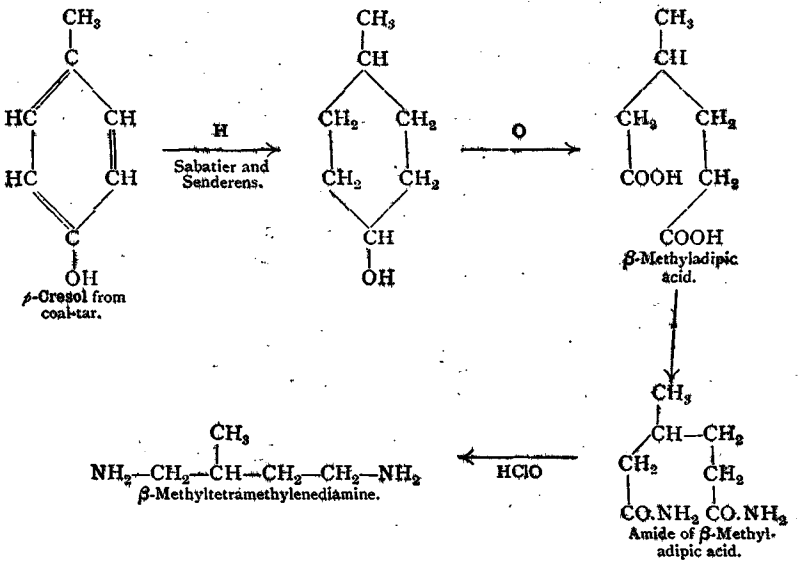


$$CH_2{=}C(CH_3){-}CH{=}CH_2 + 2N(CH_3)_3 + 2H_2O.$$

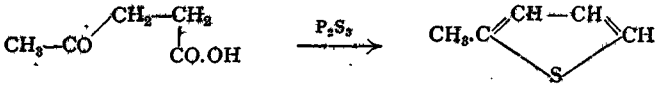
Isoprene.

Homologues of isoprene may be produced in a similar manner (see **Butadiene**, p. 366*c*).

This method really starts from **Coal-Tar**, for the β-methyltetramethylenediamine is derived from **Para Cresol** by the following series of reactions (Dr Hofmann, of Bayer & Co.) :—

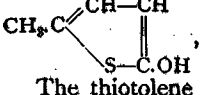


6. **Isoprene from Starch or Sugar through Laevulinic Acid.**—Heinemann (English Patent, 13,252, 1910) converts starch or sugar into laevulinic acid, $CH_3.CO.CH_2.CH_2.COOH$, by boiling with dilute HCl or H_2SO_4, and distilling the acid with phosphorus trisulphide at 130°-140° C., whereby thiotolene distils over :—



Laevulinic acid. Thiotolene.

If phosphorus pentasulphide is used in place of the trisulphide, thiotenol,



, is obtained.

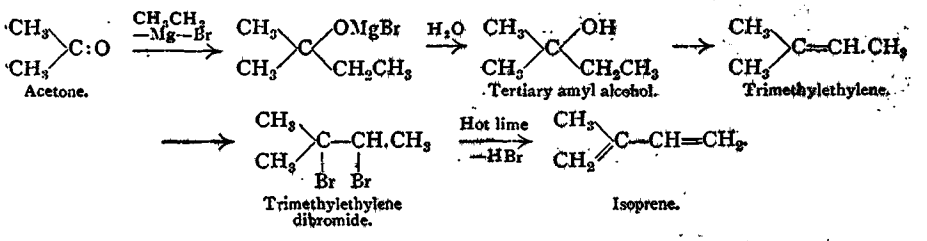
The thiotolene or thiotenol is converted into isoprene by passing either compound mixed with hydrogen over finely-divided copper or iron at a temperature of 300°-500° C. In the presence of hydrogen the sulphur is eliminated and combines

with the metal forcing a metallic sulphide, which is then reduced by the excess of hydrogen to free metal. The final product is isoprene :—

Thiotolene. Isoprene.

Above 500° C. the isoprene is converted into its polymer dipentene, $C_{10}H_{16}$.

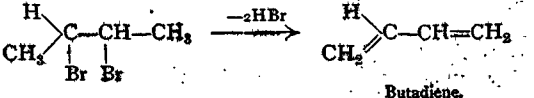
7. **Isoprene from Acetone** (compare C. Harries, *Annalen*, 1911, 383, 164).—Acetone is treated with ethyl magnesium bromide by Grignard's process, and is then transformed into tertiary amyl alcohol, thus :—



Acetone. Tertiary amyl alcohol. Trimethylethylene.

Trimethylethylene dibromide. Isoprene.

It will be remembered that in a similar manner butylene dibromide yields butadiene :—



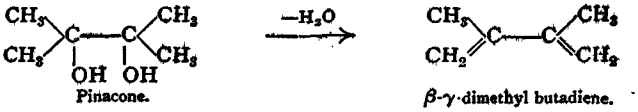
Butadiene.

Acetone is derived from **Wood Distillation** (p. 333), but is also now produced by **fermentation processes** (Fernbach) from starch.

Manufacture of β-γ-Dimethyl butadiene (Di-isopropenyl, Dipropylene)

(See Couturier, *Ann. Chim. Phys.*, 26, 485 (1892); *Bull. Soc. Chim.* (3), 33, 454 (1880); Kondakow, *Journ. Prakt. Ch.* (2), 59, 299 (1899); 62, 175 (1900), 63, 113 (1901), 64, 109 (1901). See also German Patent, 57,466, iv. 12, of the Badische Anilin- u. Soda-Fabrik, and English Patent, 2,312, 1912, of Fr. Bayer & Co., Elberfeld.)

This substance has technical importance, since Kondakow showed that it can be polymerised into a caoutchouc which is capable of vulcanisation, producing an elastic sheet of good firmness. β-γ-dimethyl butadiene can be prepared from **Pinacone**, $(CH_3)_2.C(OH)—C(OH).(CH_3)_2$, *e.g.*, by heating with dilute sulphuric acid (Couturier), or by heating pinacone dichloride with alcoholic potash (Kondakow). Technically the best way is to lead pinacone over heated potassium bisulphate (German Patent, 57,466, 1912), according to the patented method of Meisenburg and Delbrück (Fr. Bayer) :—



Pinacone. β-γ-dimethyl butadiene.

Pinacone is obtained from **Acetone** by reducing it with magnesium amalgam (Holleman, *Rec. des Pays Bas*, 25, 206 (1906); *Zentralbl.*, 1906, ii. 748) :—

Acetone. Pinacone.

Manufacture of Synthetic Rubber by Polymerising Butadiene, Isoprene and its Homologues

Butadiene, isoprene and its homologues can be polymerised into caoutchouc-like bodies by a great many methods, all of which are protected by patents.

1. **Polymerisation by Metallic Sodium.**—Polymerisation of the whole mass of butadiene or isoprene by the catalytic action of small quantities of sodium at a low temperature was discovered independently by Dr Matthews and C. Harries in 1910. The action is practically quantitative, and is not seriously affected by the presence of impurities like trimethylethylene, $(CH_3).C=CH.CH_3$, which are not capable of polymerising to rubber. The English patent was applied for by Matthews and Perkin on 25th October 1910 (English Patent, 24,790, 1910), while Harries, Bayer, & Co. applied for a similar patent three months later (English Patents, 1,125, 1911; 27,361, 1911).

In order to polymerise the isoprene to rubber it is sealed up in tubes with about 3 per cent. of thin sodium wire, and heated for several days at about 60° C. The dark brown product may be treated with acetone, which precipitates the rubber, and this may then be washed with alcohol or treated with steam to remove any unpolymerised hydrocarbon. Harries (*Liebig's Annalen*, 1911, 383, 213) showed that when butadiene was heated in a closed tube to 35°-40° C., with about 5 per cent. of sodium wire it similarly polymerised to produce an excellent rubber. From 9 g. butadiene he obtained 8 g. butadiene rubber—a practically quantitative yield—which could be vulcanised by either the hot or cold process.

Since the action is catalytic, the bulk of the sodium is recovered unchanged. The method appears to be, technically, a very important one.

2. **Polymerisation by Spontaneous Change.**—Isoprene has been observed to slowly change into rubber when kept, but the process is uncertain and too slow to be technically of importance.

3. **Polymerisation by Heating.**—Heinemann (English Patent, 21,772, 1907) heats isoprene in a sealed tube to 100°-150° C. for three days, with or without the addition of acids or alkalis or neutral catalysts. Fr. Bayer, Elberfeld (English Patent, 17,734, 1910) and G. Lilley (English Patent, 29,277, 1909) have also filed similar patents. F. Bayer (see French Patent, 433,825) polymerises by heating with anhydrides of fatty acids; *e.g.*, isoprene is heated to 150° C. with acetic anhydride.

4. **Polymerisation by Saturating with Oxygen or Ozone.**—Heinemann (English Patent, 14,041) treats the cold isoprene with oxygen or ozone for some hours, and then heats the oxidised product in a closed vessel from 40°-100° C. for many hours until the isoprene becomes viscous. The vessel is cooled and the mass freed from unconverted liquid by evaporating and precipitating the caoutchouc with alcohol.

5. **Other Methods of Polymerising.**—Sunlight, concentrated HCl, alkalis, and other similar chemicals promote polymerisation. Blood serum, albumin, starch, urea, etc., also polymerise butadiene and isoprene (see English Patents, 15,254, 1910; 1,124, 1911; 27,361, 1911).

Commercial Production of Synthetic Rubber

The synthetic rubber process of Messrs Strange & Graham (Synthetic Products Company, London) is as follows:—

The starting point is maize, potatoes, or any other cheap starch-containing substance. Five operations are needed for producing synthetic rubber from this raw material:—

Operation 1.—Fermentation of maize or potato mashes into a mixture of higher alcohols (fusel oils) and acetone by means of *Fernbach's* fermentation cultures (pp. 314, 333). Two parts of fusel oil to one of acetone is produced, and 43 per cent. of the starch is converted into these products. The acetone and the fusel oil are separated from each other and from the watery residue by simple distillation. 65 per cent. of the fusel oils consists of butyl alcohol.

Operation 2.—The fusel oils are treated with dry hydrochloric acid gas, and monochlorhydrocarbons are produced:—

$$\underset{\text{Butyl-alcohol.}}{CH_3.CH_2.CH_2.CH_2OH} + HCl = \underset{\text{Butyl chloride.}}{CH_3.CH_2.CH_2.CH_2.Cl} + H_2O$$

Operation 3.—The monochlorhydrocarbons are converted by means of chlorine into dichlorhydrocarbons in a special apparatus invented by Mr C. A. Pim, the desired product being removed from the raw material by the action of gravity, as described on p. 366*b*.

$$\underset{\text{Butyl chloride.}}{ClCH_3CH_2CH_2CH_2Cl} + Cl = HCl + \underset{\text{Butylene dichloride.}}{CH_3CHCl.CH_2CH_2Cl}$$

Operation 4.—The dichlorides are now converted into butadiene, isoprene, etc., by passing the dichlor derivatives over hot soda lime :—

$$\underset{\text{Butylene dichloride.}}{CH_3.CHCl.CH_2.CH_2.Cl} \xrightarrow[-HCl]{\text{Hot soda lime}} \underset{\text{Butadiene.}}{CH_2=CH-CH=CH_2} + HCl$$

Operation 5.—The resulting hydrocarbons are now converted into rubber by allowing them to stand in contact with a small quantity of metallic sodium (made from common salt by electrolysis) whereby the liquid gradually polymerises to solid raw rubber in a few hours or weeks, according to the temperature employed. The sodium acts catalytically, practically none being used up.

Cost of Production.—The starch in maize costs on the average less than 1d. per lb.; the only other raw materials required are: common salt costing 30s. per ton, lime costing 30s. per ton, and coal, costing 15s. per ton. The total cost of the raw materials used for making 1 lb. of rubber does not exceed 2d. It is stated that the cost of producing 1 lb. of rubber by this process will not exceed 4d. to 6d. per lb.

The other commercial processes for making synthetic rubber start from coal-tar through the phenols, or from petroleum which can be "cracked" to give rise to hydrocarbons which can be converted into isoprene or butadiene. Another promising method lies in chlorinating the lighter fractions of petroleum and then passing them over heated lime. Patents for carrying out these operations are discussed in the preceding pages. As to the cost of production by these processes no data have been published.

SECTION X

The Industry of Aliphatic Chemicals

THE INDUSTRY OF ALIPHATIC CHEMICALS

By G. Martin, Ph.D., M.Sc.

LITERATURE

Very scattered. An account of the patents will be found in Winther's "Patents der Organischen Chemie." 3 vols. 1877-1905.

ALIPHATIC ACIDS

Oxalic Acid, $H_2C_2O_4.2H_2O$

Until recently oxalic acid was obtained exclusively from **sawdust** (or other carbohydrate) by heating to 240°-260° for about six hours in iron pans with caustic alkali (40 parts KOH + 60 parts NaOH), usually in the proportion 50 parts wood to 100 parts alkali. On cooling, the material was thrown into iron filter boxes with wire-gauze false bottoms, and the substance washed with water drawn through the mass by means of a vacuum pump. The residue of sodium and potassium oxalate was heated while stirring with milk of lime in an iron pan, the caustic soda formed was drawn off and used again, while the insoluble **calcium oxalate**, after washing, was decomposed by dil. H_2SO_4 in wooden lead-lined vats, and purified by recrystallisation.

Recently (German Patent, 103,856) the heating has been carried out *in vacuo* at 180° C.—a much lower temperature. Another process (A. Droste, German Patent, 199,583) mixes the sawdust, etc., with half its weight Na_2CO_3 solution (sp. gr. 1.04-1.1), adds KOH solution of same specific gravity, stirs, and rapidly adds the theoretical amount (determined by a previous experiment) of powdered permanganate, stirs, allows to stand twelve to twenty hours, when the wood is almost completely oxidised to oxalic acid.

Manufacture of Oxalic Acid from Formates.—The recent synthetic methods of manufacturing formic acid has so lowered the price of formates that the synthetical manufacture of oxalic acid from them has become profitable, and may displace the older method. When sodium formate is heated to 360° (German Patent, 111,078) with sodium carbonate it produces sodium oxalate, thus:—

$$H.COONa + Na_2CO_3 = Na_2C_2O_4 + NaOH.$$

Recent patents (German Patents, 144,150, 161,512, 204,895) taken out by the Elektrochemische Werke, Bitterfeld, allow a better and almost theoretical yield of oxalate by mixing sodium formate with sodium oxalate and about 1 per cent. of alkali, and heating, when, apparently, the formate decomposes catalytically, thus:—

$$\begin{matrix} HCOONa \\ H.COONa \end{matrix} = \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2.$$

The formate first melts, hydrogen is evolved, and at 360° C. the mass solidifies again to a mass of technically pure oxalate in a porous condition. By heating *in vacuo* the change occurs at 280° C., and the evolved hydrogen is pumped off as fast as it is generated and used for heating purposes, etc. At the low temperatures employed there is no danger of explosion since the evolution of gas ceases instantly when the vacuum is broken.

The Acid Oxalates of Potassium (salts of sorrel, salts of lemon, KHC_2O_4 and $KHC_2O_4.H_2C_2O_4.2H_2O$) are made by adding potassium carbonate to a suitable amount of oxalic acid and crystallising. Valuable domestic detergents.

Antimony Potassium Oxalate, $K_3Sb(C_2O_4)_3.6H_2O$, is used as a substitute for tartar emetic in calico printing.

Uses.—Acid potassium oxalate, $COOH.COOK.H_2O$, is much used as a **mordant** for cloth printing and dyeing; oxalic acid itself is used for whitening leather, for metal polishing powders, for removing ink-stains and iron mould from cloth, for bleaching stearine and straw (for hats), for dissolving Prussian blue in ink-making (see **Inks**), etc. etc.

Statistics.—The German *exports* of oxalic acid and salts are shown by the following figures: 1909, 44,709 dz.; 1908, 51,787 dz.; 1907, 46,827 dz.*
Of these amounts the following countries received:—

	1909.	1908.	1907.
	Dz.	Dz.	Dz.
U.S.A.	20,850	26,368	20,681
Great Britain	5,478	4,578	8,111
France	4,224	5,351	4,241

The German *import* in 1909 was only 17 dz.
The United States *imported* in 1910, 4,833,000 lbs. (value $280,000), and in 1909, 9,800,000 lbs. (value $621,000).

Formic Acid, H.COOH

Formerly formic acid was obtained by heating oxalic acid with glycerol. It is now prepared exclusively by passing carbon monoxide (CO) under 6-7 atmospheres over a mixture of calcined sodium carbonate and dry slaked lime, heated to 100°-170° C.:†—

$$Na_2CO_3 + Ca(OH)_2 + 2CO = 2H.COONa + CaCO_3.$$

Goldschmidt's process consists in heating sodium hydrate to 150°-170° C. with carbon monoxide under 6-7 atmospheres presence. Yield theoretical.

To obtain the free acid the sodium formate was formerly distilled with concentrated sulphuric acid, whereby much acid was destroyed. It has been recently proved (German Patent, 193,509) by the Chemische Fabrik Grünan, Landshoff and Meyer, that acid sodium sulphate, $NaHSO_4$, may replace the sulphuric acid with advantage, since it does not decompose formic acid, and is a cheap by-product of the alkali industry. The technical sodium formate is thoroughly mixed with finely powdered sodium bisulphate, $NaHSO_4$ (90 per cent.), and heated in retorts provided with stirring apparatus. A 97-98 per cent. formic acid distils over, while there remains in the retort a mass of finely powdered normal sodium sulphate, Na_2SO_4. Aqueous solutions of formic acid are concentrated by distillation in columnar stills. A special still for continual distillation has recently been patented by Hamburgher (German Patent, 206,902).

Anhydrous Formic Acid is prepared from dilute aqueous solutions by neutralising with lead carbonate, drying the lead formate, and decomposing in retorts (heated by hot water to 100° C.) in a stream of H_2S. PbS remains behind

* 1 dz. = 100 kg. = $\frac{1}{10}$ ton.
† German Patents, 212,844, 179,515, 209,417, 212,641.

and anhydrous formic acid distils over, containing some dissolved H_2S, from which it is freed by redistilling over lead formate. Distilling Na formate with $NaHSO_4$, as described above, yields an almost 100 per cent. formic acid.

Uses.—Since its cheapened production, its use in industry increases rapidly, as it combines the properties of an aldehyde, a moderately strong acid, and a powerful reducing agent. It can consequently be used for a great many different purposes. It finds its chief application in the dyeing industry (especially in wool dyeing) where it is replacing acetic and lactic acid, and acid potassium tartrate (argol). Large quantities of formates are now used for making oxalic acid. It is also used as an antiseptic for preserving fruit juices; in brewing it is added to the mash, where it stimulates the fermentative power of the yeast, preserves the diastase in the malt, and prevents certain acid-producing bacteria from developing; also used in tanning.

Statistics.—The United States imported in 1909, 809,000 lbs. (value $57,000), and in 1910 770,000 lbs. (value $54,000) of formic acid.

For **Acetic Acid** see under **Vinegar** and under **Wood Distillation.**

Tartaric Acid, COOH.CH(OH).CH(OH).COOH

LITERATURE

RASCH.—"Die Fabrikation der Weinsauer." Berlin, 1897.

STIEFEL.—"Das Raffinieren des Weinsteins und die Darstellung der Weinsteinsaure." Vienna, 1894.

DAMMER.—"Technologie der Neuzeit." Bd. I., 662. 1910. (Dr Emde.)

ALLEN.—"Commercial Analysis." Vol. i. 1909.

Four varieties of tartaric acid exist, viz., dextro, laevo (which rotate the plane of polarised light to the right or left, respectively), optically inactive racemic acid (decomposable into the above acids), optically inactive mesotartaric acid (not so decomposable).

The only important commercial variety is the dextro-rotatory variety—ordinary tartaric acid.

Manufacture of Tartaric Acid from Wine Lees.—Formerly the main raw product for the manufacture of tartaric acid was crude **Argol** or **Tartar**—the potassium salt of tartaric acid. Now the greater part is made directly from the wine lees itself. In the winter months there gradually settles out at the bottom of the fermenting wine vats a deposit consisting of yeast cells, acid potassium tartrate, grape husks, etc. etc. When the wine is run off this mass is removed, pressed between filter cloths to remove excess of wine, then rapidly dried either in simple drying chambers, or in the air itself. It is then sold to the tartaric acid factories.

The composition of lees is greatly altered by the habit, prevalent in Spain, of "plastering" the wine by adding to the wine an impure calcium sulphate, whereby the tartrate is converted principally into **calcium tartrate**, instead of remaining as acid potassium tartrate.

The composition of some typical wine lees, as imported for manufacture, is shown by the following table by Warington:—

WINE LEES.

	Spanish Wine Lees. I.	Spanish Wine Lees. II.	French Wine Lees.
Tartaric acid as acid tartrate	5.27	22.66	4.48
Tartaric acid as neutral tartrate	19.13	11.67	21.34
Total tartaric acid	24.40	34.33	25.82
Water (at 100° C.)	10.694	9.750	11.305
Sand	4.900	4.600	4.600
Alumina	0.832	0.578	0.844
Iron oxide	0.351	0.214	0.394
Lime	10.600	4.514	10.567
Magnesia	0.363	0.209	0.327
K_2O	2.123	...	1.868
Na_2O	0.060	...	0.100
P_2O_6	0.486	0.569	0.527
CO_2	0.388	...	0.435
Anhydrous tartaric acid	21.472	30.210	22.721
Organic matter	34.448	33.672	37.952

The great difficulty in working wine lees for tartaric acid arises from the fact that a slimy mass is produced on adding water or acid, which renders filtration difficult. Again only small amounts of tartaric acid (22-30 per cent.) are present, and consequently a very bulky residue remains after extracting the tartaric acid. The method now most largely used is **Rasch's Neutral Process** (German Patent, 92,650).

The liquid or pasty lees is placed in a rotating closed cylindrical chamber A, which is heated externally by a steam jacket to 100°-120° C. Within it are a number of heavy balls K, thus giving the chamber the function of a ball mill. The lees are dried by the heat, and all bacteria and spores killed; at the same time the rolling balls grind it up into a fine dust, while any wine or volatile oils present in the lees distil away through the pipe B and may be recovered, or if evil smelling burnt in a furnace. The process takes three hours. The dry powdered lees are now placed in a wooden vat provided with stirring apparatus, cold water from a previous operation is added (1,500-1,800 kg. lees require 80 hl. water), and the whole is well stirred. Next the calculated amount of calcium chloride solution necessary to form an insoluble calcium salt with the tartaric acid is run into the rapidly stirred mass, and then lime water gradually run in until the solution is exactly neutralised, which is tested with litmus. The process of neutralisation takes three hours. The temperature must not exceed 25° C. After stirring for a couple of hours longer the precipitate of calcium tartrate is allowed to settle, and the supernatant water drawn off. More water is added, the whole mass stirred up again for one hour, allowed to settle, and again the water is drawn off. This process is repeated eight times or so. The precipitate now left in the vat has added to it sufficient sulphuric acid to decompose all the calcium tartrate present and in addition to provide an acid solution, which prevents fermentation of the—$CaC_4H_4O_6 + H_2SO_4 = CaSO_4 + C_4H_6O_6$.

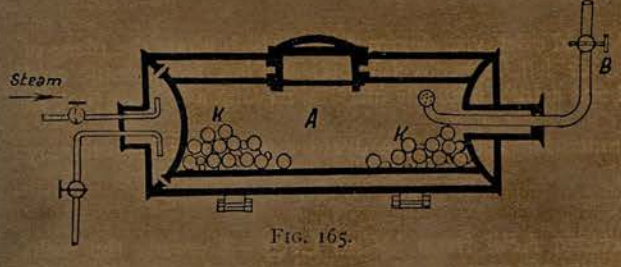


FIG. 165.

The solid and liquid contents of the vat are then passed through the filter press, the expressed fluid, of sp. gr. 10° Bé., containing the free tartaric acid is run into

crystallising pans, and there evaporated for tartaric acid. The first washings of the pressed cake are usually added to the tartaric acid filtrate and evaporated with this. The second wash water, however, is run back into the vat and used with a fresh lot of lees.

If the colouring matter of the wine lees has been previously rendered insoluble by treating the moist lees with 1-2 per cent. of formaldehyde and drying as above, the mother liquors yield on evaporation the first time a crop of white crystals (German Patent, 194,812). The first evaporation is carried out in large wooden vessels lined with lead, heated by leaden steam pipes, and provided with stirring apparatus. The liquid is concentrated to 25° Bé., the precipitated $CaSO_4$ is filtered off, and the tartaric acid allowed to crystallise. All mother liquors over 25° Bé. must be concentrated in vacuum evaporators as not only is heavy loss avoided but better products of crystallisation are attained; the mother liquors when sufficiently concentrated are run out into large crystallising pans. The mother liquors for crystallising should contain 60-90 g. H_2SO_4 per litre. When necessary the mother liquors are decolourised with bone charcoal (previously extracted with HCl) and potassium ferrocyanide. Sometimes, but only in exceptional cases, H_2S or CaS is added to get rid of lead. When the tartaric acid is for edible purposes evaporation is carried out in earthenware vessels, thus avoiding the introduction of lead into the product.

Manufacture of Tartaric Acid from Argol, Crude Tartar, or Cream of Tartar.—Before the method of working wine lees for tartaric acid was understood, almost all the tartaric acid of commerce was obtained from this source. It is now principally used for making potassium tartrate.

Argol or crude tartar is the crystalline crust deposited on the sides of the vessels used for fermentation. It contains 40-70 per cent. tartaric acid, principally as potassium hydrogen tartrate, $KH.C_4H_4O_6$. Its deposition is favoured by the fact that the salt is but sparingly soluble in dilute alcohol. Very low grade **Argols** resemble superior **wine lees**, while best quality **Argols** may equal ordinary refined tartar. **Cream of tartar** or **refined tartar** is obtained by boiling crude argol with water, filtering, and crystallising.

To obtain tartaric acid the crude tartar is boiled with water containing chalk, whereby half the tartaric acid is converted into insoluble calcium tartrate:—

$$2KHC_4H_4O_6 + CaCO_3 = CaC_4H_4O_6 + K_2C_4H_4O_6 + CO_2 + H_2O.$$

Calcium sulphate is then added, whereby the remainder of the tartaric acid is precipitated as calcium tartrate:—

$$K_2C_4H_4O_6 + CaSO_4 = CaC_4H_4O_6 + K_2SO_4.$$

The precipitated calcium tartrate is strained through a sieve, filter pressed, washed, and converted into tartaric acid by treating with sulphuric acid, the $CaSO_4$ being deposited and the solution of tartaric acid being drawn off and boiled down for tartaric acid crystals as previously described:—

$$CaC_4H_4O_6 + H_2SO_4 = CaSO_4 + C_4H_6O_6.$$

Properties.—Ordinary tartaric acid is soluble in 0.7 part of cold water and 0.5 part of boiling water; its aqueous solutions are gradually decomposed from the growth in them of fungus. Calcium sulphate, lead, and free sulphuric acid may be present in commercial tartaric acid.

Uses.—By far the largest quantity of tartaric acid is consumed in the dyeing and calico-printing industries, being there used as a mordant, especially in the form of tartar emetic, $K(C_4H_4(SbO)O_6$. It is also used for effervescing medicines, baking powders, etc., also as a preservative for albumen, glue, gelatine, jellies, etc., for medicines, and for making chrysamine.

Tartar Emetic, Potassium Antimonytartrate, $K(SbO)C_4H_4O_6\frac{1}{2}H_2O$, made by making 3 parts of Sb_2O_3 and 4 of cream of tartar into a thin paste with water, digesting on the water bath for thirty minutes, adding 8 parts of water, boiling, and filtering while hot. Octahedral crystals, soluble in 14.5 parts of cold and 1.9 parts hot water. Used as a mordant in dyeing and calico printing, also in medicine.

Statistics.—The German import of tartaric acid amounted to: 1909, 3,241 dz.; 1908, 2,816 dz.; 1907, 2,525 dz.

In the same time she exported: 1909, 19,076 dz.; 1908, 17,259 dz.; 1907, 15,289.

Great Britain received of this amount: 1909, 11,260 dz.; 1908, 9,484 dz. (1 dz. = 100 kilos = about $\frac{1}{10}$ ton).

The total import of **tartaric acid** and **cream of tartar** into Great Britain is shown by the following figures:—

Tartaric Acid.—1906, 36,779 cwt.; 1910, 44,584 cwt.; value in 1910, £203,365.

Cream of Tartar.—1906, 64,287 cwt.; 1910, 81,983 cwt.; value in 1910, £307,000.

The *export* from Great Britain in 1910 was 2,000 cwt. (value £8,000) of **cream of tartar**, and 7,600 cwt. (value £31,000) of **tartaric acid.**

The United States imported in 1910, 28,400,000 lbs. (value $2,232,000) of tartar, and 104,000 lbs. (value $16,000) of tartaric acid.

Citric Acid, $COOH.CH_2.C(OH)(COOH).CH_2.COOH$,

Occurs in the acid juices of many fruits; it is obtained commercially from the lemon, the lime, and the bergamot by pressing the fruit, concentrating the

expressed juice, heating nearly to boiling and running in, with constant stirring, a mixture of chalk and water. Calcium citrate is formed, and being more difficultly soluble in hot than in cold water, is precipitated. After filtering and washing, the crude calcium citrate is then decomposed with sulphuric acid similarly to the calcium tartrate in the manufacture of tartaric acid. Expressed lemon juice is a practically pure solution (6 per cent.) of citric acid and is the best raw material. The juice, however, is concentrated to 60 per cent. citric acid before treating with chalk.

The following table (after Warrington) shows the amount of acid met with in the various citric juices which occur in commerce :—

	Specific Gravity.	Acid.	Combined Organic Acid.
		Oz. per Gallon.	Oz. per Gallon.
Lemon juice, raw - - -	1.035-1.040	10.6-13.5	0.4-0.7
,, concentrated -	1.28-1.38	82-112	8-6
Lime juice, raw English - -	1.04-1.05	11-13	0.3
,, raw Sicilian - -	...	6-9	0.85
,, concentrated - -	1.20-1.25	56-72	6-8
Bergamot juice, concentrated -	1.22-1.25	47-55	7-8

It is interesting to note that an organism, *Mucor piriformis* (see German Patent, 72,957, C. Wehmer), is known which ferments **sugar** directly into citric acid; lemon juice, however, is produced so cheaply in Sicily that no wide technical application of this fact has yet been made.

Citric acid was formerly frequently adulterated with the cheaper tartaric acid. For detection of the adulteration see Allen's "Commercial Analysis," vol. i. p. 588 (1909).

Commercial citric acid often contains sulphuric acid and lead. To free from lead it is treated with H_2S, completing the crystallisation in non-leaden vessels.

Properties.—Crystallises in colourless prisms with 1 molecule H_2O. Dissolves in three-fourths part of cold water or one-half part of hot water; melts, 70°-75° C.

Statistics.—*German imports:* 1909, 3,990 dz.*; 1908, 5,537 dz.; 1907, 4,481 dz. *German exports:* 1909, 3,668 dz.; 1908, 4,537 dz.; 1907, 3,566 dz.

The quantity of lime and lemon juice imported into Great Britain in 1910 was: 685,557 gals. (value £84,455).

The United States in 1910 imported 142,000 lbs. (value $41,000) of citric acid, lemon and lime juice to the value of $65,000, and no less than 4,140,000 lbs. of calcium citrate (value $568,000).

For the manufacture of **Lactic** and **Butyric Acids** see under **Fermentation Industries**, p. 315.

Preparation of the more common Aliphatic Chemicals

II. ALDEHYDES

Aldehydes are produced by oxidising primary alcohols: thus :—

$$R.CH_2OH + O = R.C\begin{matrix}O\\H\end{matrix} + H_2O.$$

Primary alcohol. Aldehyde.

Of the numerous aldehydes known we will only consider two, viz., Formaldehyde and Acetaldehyde.

* 1 dz. = 100 kilos = about $\frac{1}{10}$ ton.

Formaldehyde, H.CHO,

Is at ordinary temperatures a pungent smelling gas condensing to a colourless liquid at $-21°$ C. It usually occurs in commerce either dissolved in water, when the solution is called "**Formaline**," or else in a solid polymerised form, $(HCHO)_3$ known as "**Trioxymethylene**."

1. **Manufacture from Methyl Alcohol.**—The aqueous solution (35-40 per cent.) is usually made by passing a mixture of methyl alcohol vapour and air, obtained by warming the methyl alcohol to 50° and drawing a rapid stream of dry air through it over "contact" substances, such as platinum, coke, copper salts, unglazed porcelain, etc., maintained at a low red heat. The methyl alcohol is oxidised to formaldehyde. The vapours pass into a number of condensing chambers arranged in series; in the first two chambers, which are empty, a 35-40 per cent. solution of formaldehyde ("formaline") is deposited, which may be freed from a little unchanged methyl alcohol by distillation.

In the other condensers a very weak aqueous solution of formaldehyde collects which is ultimately brought up to the correct strength by the passage of the methyl alcohol vapour. The reaction is:—$CH_3OH + 2O = H.CHO + H_2O$.

2. **Manufacture from Methane Gas.**—Several patents have been taken out recently for manufacturing formaldehyde cheaply from marsh gas, coal gas, coke-oven gas, or in fact any gas containing a considerable amount of methane.

G. Glock's Patent (German Patent, 109,014) consists in passing a mixture of methane, CH_4 (or a gas containing methane, such as coal gas), and air or oxygen in amount insufficient for complete combustion over red-hot "contact" agents, such as pumice, copper, asbestos, etc., a mixture of pumice and copper being especially efficient. The *Sauerstoff- und Stickstoff-industrie Hansmann & Co.* (German Patent, 214,155) use as the "contact agent" merely bark (either in lumps or ground), tar, or similar material. Here the temperature of formation is reduced from the 600° C. or so, necessary in the case of other contact agents, to 30°-50° C. The yield is 4.7 per cent. of theory, and it is proposed to use waste natural gas for the purpose. Methyl alcohol and formic acid are simultaneously produced.

Moest (German Patent, 138,442) electrolyses a solution of sodium acetate and sodium perchlorate, and obtains at the anode 60 per cent. of the theoretical yield of formaldehyde and methyl alcohol (1 : 2). The Bad. Anilin- und Soda-Fabrik, Ludwigshafen (German Patent, 185,932), pass a mixture of **formic acid vapours** and hydrogen gas over heated metals, such as iron, nickel, tin, lead, etc., or other catalytic agents.

Goldschmidt (German Patent, 183,856) passes the vapour of formic acid over moderately heated tin oxide (180° C.). Tin formate is formed, which, at the temperature employed, breaks up into formaldehyde, CO_2, and tin oxide. Most of the formaldehyde at once condenses to **paraformaldehyde** which is easily obtained pure by sublimation, and the method, therefore, is a convenient one for the manufacture of **paraformaldehyde**. A considerable amount of **methyl formate**, $H.COOCH_3$, is simultaneously produced, and is used either as such, or split by hydrolysis into methyl alcohol and formic acid.

Paraformaldehyde is usually made by evaporating an aqueous solution of formaldehyde. It then remains as a white amorphous mass, $(HCHO)_n$, which on drying passes into **trioxymethylene**, $(HCHO)_3$. This body volatilises between 180°-200° C., turning into formaldehyde again. It is sold in the form of pastilles.

Uses.—Formaldehyde is used in very large quantities as a disinfectant, especially of rooms. It is used as a preservative for crude, raw products in tanneries, knackers' yards, soap works, etc. It is often added to gums, glues, or starch solutions for a similar purpose. It is also used extensively in many industries, such as in leather making, in the indiarubber goods industry, in photography, etc. etc. It forms an insoluble compound with gelatine, and condenses with phenols, etc., to form bone substitute, etc. It is also used by gardeners to protect plants from parasites.

The **Formaline** of commerce contains about 35 per cent. of formaldehyde, and has a sp. gr. 1.079-1.081, as is shown by the following table:—

SPECIFIC GRAVITY OF FORMALDEHYDE SOLUTION (FORMALINE) AT 18.5° (Zülke)

Per Cent. HCHO.	Specific Gravity.	Per Cent. HCHO.	Specific Gravity.	Per Cent. HCHO.	Specific Gravity.	Per Cent. HCHO.	Specific Gravity.
1	1.002	11	1.027	21	1.052	31	1.076
2	1.004	12	1.029	22	1.055	32	1.077
3	1.007	13	1.031	23	1.058	33	1.078
4	1.008	14	1.033	24	1.061	34	1.079
5	1.015	15	1.036	25	1.064	35	1.081
6	1.017	16	1.039	26	1.067	36	1.082
7	1.019	17	1.041	27	1.069	37	1.083
8	1.020	18	1.043	28	1.071	38	1.085
9	1.023	19	1.045	29	1.073	39	1.086
10	1.025	20	1.049	30	1.075	40	1.087

Statistics.—The United States imported in 1910, 34,000 lbs. of formic acid (value $9,000).

Acetaldehyde, $CH_3.CHO$,

Is largely manufactured from the first runnings of rectifying stills in the manufacture of spirits. It is formed by the oxidation of alcohol; when crude alcohol is purified by treating with animal charcoal a considerable amount of acetaldehyde is produced. Acetaldehyde is sometimes manufactured by oxidising alcohol (3 parts) with $K_2Cr_2O_7$ (3 parts) and 16 parts of H_2SO_4 solution (25 per cent.). The acetaldehyde (B.P. 21° C.) distils from the mixture, and is absorbed by dry ether; then dry NH_3 gas is led into the ethereal solution and the aldehyde separated as aldehyde ammonia. This, when distilled with dil. H_2SO_4, yields acetaldehyde, which is dehydrated over $CaCl_2$.

Properties.—Colourless, mobile liquid with a peculiar odour. B.P. 20.8° C.; M.P. −120° C.; D_0 0.8009. Mixes in all proportions with water and alcohol.

Uses.—For making quinaldine, quinoline yellow, hydrazine, etc.

Paraldehyde, $(CH_3CHO)_3$, a liquid polymer of acetaldehyde (obtained by treating acetaldehyde with small quantities of acids or salts—such as HCl, H_2SO_4, $ZnCl_2$, etc.—at ordinary temperatures), finds some application in medicine as a sleep inducer.

III. ALCOHOLS

For the manufacture of **Methyl Alcohol**, see under **Wood Distillation**. For **Ethyl Alcohol** see under **Spirits**. For **Butyl** and **Amyl Alcohol** see under **Fusel Oils**, p. 314.

IV. HALOGEN DERIVATIVES

Methyl Chloride, CH_3Cl,

Is obtained from the residues of beetroot molasses, p. 163, by distillation with lime. The aqueous distillate is neutralised with HCl and the methyl alcohol distilled off. The residual liquor is then concentrated, NH_4Cl crystallises out, while the mother liquors contain **trimethylamine chloride,** $N(CH_3)_3.HCl$. These are evaporated to dryness and heated to 350° C. with HCl under pressure, when methyl chloride is formed: $(CH_3)_3N.HCl + 3HCl = 3CH_3Cl + NH_4Cl$. (Vincent, see *Ding. Pol. J.*, 230, 272; "Jahresber.," 1878, 1135.) *Weinland & Schmid* ("Ber." (1905), 38,

2327) show that dimethylsulphate readily yields CH_3Cl when allowed to flow into a warm very concentrated solution of KCl:—

$$KCl + (CH_3)_2SO_4 = CH_3Cl + K.(CH_3).SO_4.$$

To purify the gaseous CH_3Cl, it is washed with water, dried with concentrated H_2SO_4, and condensed to a liquid in strong steel cylinders.

Properties.—*Gas;* sweet odour; B.P. −24° C.; M.P. −103° C. Used in making aniline colours; also for producing cold.

Ethyl Chloride, C_2H_5Cl, and Ethyl Bromide, C_2H_5Br,

Are manufactured by mixing concentrated H_2SO_4 (2 parts) with 96 per cent. alcohol (1 part), and, after standing, diluting with water (½ part), adding KCl or KBr (1 part) and distilling. Ethyl chloride, B.P. 12.5° C., is used as a local anæsthetic; it produces great cold when it evaporates. **Ethyl Bromide**, B.P. 38° C. This preparation is used as an anæsthetic. Crude commercial ethyl bromide is now made by allowing 6 parts of bromine to slowly flow into a mixture of 1 part red phosphorus and alcohol, shaking and cooling continually during the operation. It always contains traces of poisonous phosphorus compounds.

109 gals. (value £534) of ethyl chloride and 77 gals. (value, £13) of ethyl bromide were imported into England in 1910. The duty on **ethyl chloride** is £1. 1s. 10d. per gallon, and on **ethyl bromide** 1s. 5d. the lb. See also **General Anæsthetics.**

The import into the United States was 5,800 lbs. (value $4,900) in 1910. Duty 30 per cent.

Chloroform, $CHCl_3$

1. **Manufacture by Heating together Alcohol and Bleaching Powder.**—The action is complex, chloral (see under) being first formed, which decomposes in the presence of the calcium hydrate of the bleaching powder into chloroform and calcium formate. Aldehyde is simultaneously produced:—

$$\underset{\text{Calcium hypochlorite.}}{4Ca(OCl)_2} + \underset{\text{Alcohol.}}{2C_2H_5(OH)} = \underset{\text{Chloral.}}{2CCl_3.CHO} + CaCl_2 + 3Ca(OH)_2 + 2H_2O$$

$$\underset{\text{Chloral.}}{2CCl_3.CHO} + Ca(OH)_2 = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcium formate.}}{Ca(HCO_2)_2}$$

300 kg. of 96 per cent. alcohol and 1,300 l. of water are placed in iron boilers 1.40 m. in height and 2 m. in diameter, provided with powerful stirring apparatus, a man-hole (for charging with bleaching powder), inlet tubes for steam and water, and, in the cover, a tube for leading away the evolved vapours into the condenser, which consists of a copper spiral immersed in cooling water. Now 400 kg. of bleaching powder, containing 20-22 per cent. available chlorine, is gradually added while the stirring apparatus is in rapid action, the man-hole closed, and the vessel heated by steam until the temperature reaches 40° C. The steam is then shut off, but the temperature continues to increase. When it reaches 45° C. the stirring is stopped. At 60° C. the action reaches a maximum, and any further temperature increase is prevented by running cold water over the generator. A glass tube let into the leading tube as it comes from the condenser to the collector allows the operator to see at this stage a fine rain of chloroform, water, and alcohol blowing through the outlet tube into the vessel for collecting the distillate.

This vigorous action lasts for about a minute, and then chloroform begins to distil over in a rapid stream, and is received in tinned iron vessels. The issuing air, saturated with $CHCl_3$ vapour, is caused to bubble through water, and is thus freed from chloroform. When about 30 kg. of $CHCl_3$ have distilled over, the stirring apparatus is again set in action until the distillate ceases to separate out into two layers, the heavy chloroform being underneath. At this stage the receiver is changed, and the distillation continued until the distillate ceases to give a turbidity with water, when it contains no more chloroform. The receiver is again changed until the distillate acquires the density 3° Tralles. The operation is then stopped, the lime being run off through a valve placed in the bottom of the generator. *Yield,* 31-31.5 *kg.* **Chloroform.** The dilute alcohol distilled over is mixed with the requisite amount of alcohol to make it of the same composition as the original alcoholic charge, and is used again for repeating the operation with a new charge of bleaching powder.

The chloroform contains alcohol and ether; it is purified by rectification. When it is to be used as an anæsthetic, the commercial chloroform is washed in

succession with distilled water, with dilute (2.5 per cent.) H_2SO_4 (for two to three days); with a 3 per cent. solution of NaOH, and finally again with distilled water; it is dried over fused $CaCl_2$, a small amount of poppy-seed oil added, the whole distilled, and the distillate, which should boil at 61° C., is mixed with 2 per cent. of pure absolute alcohol. This is done because $CHCl_3$, especially under the action of light, undergoes a slow spontaneous decomposition, with formation of chlorine and the poisonous phosgene gas, $COCl_2$ (to whose influence many fatal accidents have been traced); the addition of a small percentage of alcohol increases the stability of chloroform. The chloroform is kept in stout bottles with ground glass stoppers, rendered air-tight with chromatised gelatine. Pictet purifies $CHCl_3$ by freezing at − 70° C. to − 100° C., and centrifugalling the crystalline mass from the impure liquid portions.

2. **Manufacture from Acetone and Bleaching Powder.**—The process is much the same as with alcohol, but the yield is better, 100 kg. acetone giving 175 kg. $CHCl_3$. 270 parts of bleaching powder are mixed with 800 parts of water, and gradually added to 22 parts of acetone and 70 parts of water. $CHCl_3$ is generated, with the evolution of heat, and distils off. Towards the end of the reaction, a gentle external heating is applied.

3. **Manufacture by Besson's Continuous Process.**—By this process (German Patent, 129,237) chloroform is obtained from alcohol in almost theoretical quantity, and in an extremely pure state; moreover, the process has the great advantage of being a continuous one. Alcohol, as free from water as possible, is chlorinated by dry chlorine gas until the chlorination product attains a density of 25°-35° Bé., or even more, whereby chloral hydrate or a similar body is produced. The chlorinated alcohol is now treated with milk of lime or other caustic alkali with gentle heating, when pure chloroform is evolved, probably according to the equation:—$CCl_3.CO.H + NaOH = CHCl_3 + HCOONa$.

Fig. 166 illustrates Besson's apparatus:—

A stream of alcohol slowly runs from *c* into the vessel *a*, flowing in succession over a number of shallow trays *b*, placed one below the other as seen in the figure. A stream of dry chlorine gas enters by *d*, meets the stream of flowing alcohol, saturates it, and escapes through *h*. The chlorinated alcohol collects in the holder *e* and thence pours into the funnel-like base of the chlorinator *a*. Fragments from the vessel—*e.g.*, lead chloride, etc., produced by the destructive action of chlorine on the leaden walls—can be run off into *g*. *k* are steam coils for producing the necessary degree of warmth for the chlorination to take place most readily. The chlorinated alcohol, together with any vapours (which are condensed in *j*) flow through a cooler *j* up the tube *o* into the vessel *m*, which is charged with bleaching powder. The mixture is slowly forced thence, by means of a screw worm, through *q* into the large chamber *l*, also containing a screw worm *r* and steam heating coils *s*. A stream of milk of lime is slowly forced into the apparatus from *n*, and the worm *r* slowly mixes and forces the mass along the chamber *l* and out through *t*. The chloroform vapours escape through tubes *w* in the cover of the apparatus, through *x* into the condenser *p*, or direct into a rectifying apparatus.

It is stated that 100 parts of alcohol yield from 95-105 parts of pure chloroform.

4. Among other methods of manufacturing chloroform may be mentioned: (*a*) the electrolysis of an alcoholic solution of $CuCl_2$ (not a commercial success up to the present): (*b*) by distilling pure chloral with NaOH:—$CCl_3.CHO + NaOH = CHCl_3 + HCOONa$ yields a very pure product; (*c*) when **salicylide**, $\left(C_6H_4\overset{O}{\triangle}CO\right)_4$—an anhydride produced by warming salicylic acid with phosphorus oxychloride—is dissolved in crude chloroform, it crystallises out with two molecules of $CHCl_3$. On distilling the crystals on the water bath perfectly pure $CHCl_3$ distils over, leaving behind the **salicylide** to be used again for another operation. (Anschütz.)

Properties.—Colourless liquid, with sweetish pleasant taste and smell. B.P. 61.5° C.; D_{15}, 1.5008. When used as an anæsthetic contains 2 per cent. alcohol.

For further information see under **Anæsthetics**, p. 602.

Uses.—Largely in medicine as an anæsthetic. Technically it is used as a solvent, especially for rubber, gutta-percha, etc. Also as a cleansing agent.

Statistics.—*German exports* of $CHCl_3$: 1908, 1,300 dz.: 1909, 1,480 dz. (1 dz. = 100 kilos = $\frac{1}{10}$ ton.)

The English import of chloroform was 1,774 lbs. (value £299), and the export 1,531 lbs. (value £158) in 1910. The duty on chloroform is 4s. 4d. the lb.

The United States imported in 1910, 967 lbs. of chloroform (value $1,400). The American duty is 10 cents the lb.

Chloral, $CCl_3.CHO$; Chloral Hydrate, $CCl_3.CH(OH)_2$

Manufacture.—A slow stream of dry chlorine gas is led into 96 per cent. alcohol, at first in the cold, but afterwards with gentle warming (60° C.), until HCl ceases to be evolved. 7 kg. alcohol require two weeks for complete chlorination. The action is complex, but finally chloral, $CCl_3.CHO$, is formed as a heavy oil. It is purified by treating with concentrated H_2SO_4, then distilled from H_2SO_4, dried and rectified, the part passing over between 94°-95° C. being pure chloral. It forms an oily liquid, with a penetrating smell. D_0, 1.541; B.P. 97° C. On keeping it passes into solid **metachloral.**

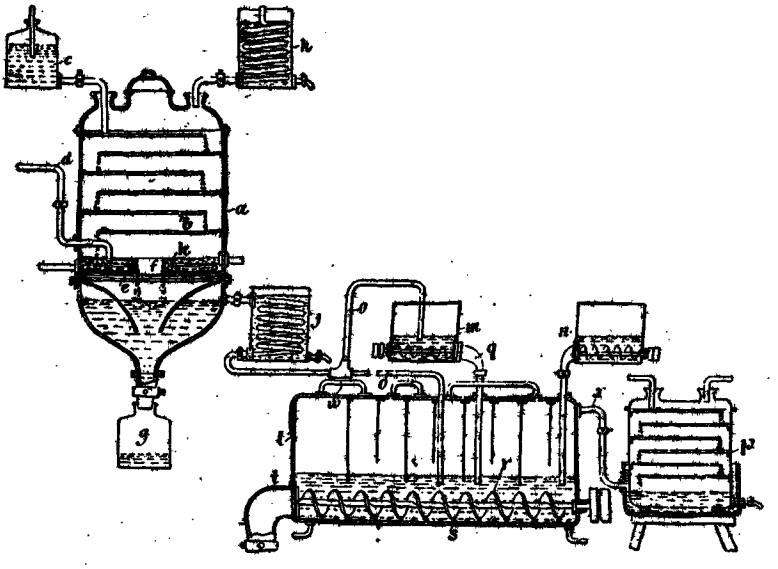


FIG. 166.—Besson's Process for the Manufacture of Chloroform.

To produce **chloral hydrate** 100 parts of chloral are mixed with 12.25 parts of water, when combination ensues and a mass of large monoclinic crystals are produced. Chloral hydrate heated with alkalis yields pure $CHCl_3$. Heated to 57° C. it decomposes to chloral and water. It is used in medicine as a sleep producer, but is now being replaced by other more efficient drugs. (See **Hypnotics**, p. 608).

The English duty on chloral hydrate is 1s. 9d. the lb. The English import of chloral hydrate was 20,000 lbs. (value £3,400) in 1906, and 28,800 lbs. (value £2,760) in 1910.

The American duty on chloral hydrate is 55 cents. per lb. (1910). The United States in 1910 imported 171,000 lbs. (value $152,000).

Polychlorals, $(CCl_3.CHO)_x$ (see **Hypnotics**, p. 608),

are produced by treating chloral with amines (such as pyridine) or chloral hydrate with concentrated H_2SO_4 (see German Patents, 165,984, 170,534). They are soluble in water and are used as anæsthetics and hypnotics.

Dormiol,

A liquid soporific, is chloralamylalcoholate, $CCl_3.CH(OH).OC_5H_{11}$, produced from chloral and amyl alcohol.

Hypnal,

Similarly produced from chloral hydrate and antipyrine, has the formula:—

$$C_{11}H_{12}N_2O.CCl_3.(OH)_2.$$

Dimethylethylcarbinolchloral, $Cl_3.CH(OH).O.C(CH_3)_2.C_2H_5$,

Is produced by warming to 60° a mixture of chloral hydrate and amylene hydrate, $C_2H_5.C(CH_3)_2.OH$.

Chloralformamide, $CCl_3.CH(OH).NH.CHO$,

Is similarly produced from chloral and formamide.

Chloralacetonechloroform, $CCl_3.CH(OH).O.C(CCl_3).(CH_3)_2$,

Is similarly produced from acetone chloroform and chloral hydrate (German Patent, 151,188). A valuable local anæsthetic and hypnotic.

Iodoform, CHI_3

Iodoform was formerly exclusively made by warming alcohol or acetone with iodine and caustic soda or alkaline carbonate; more recently Dr Marius Otto (German Patent, 109,013) made it by simply leading ozone into a mixture of potassium iodide (55), sodium carbonate (10), alcohol (300), water (100), warmed to 50° C. By far the greater part, however, is now made electrolytically, a very pure product being thus obtained (Elbs and Herz, *Zeit. f. Elektroch.*, 1897, 4, 113; Förster and Mewes, *loc. cit.* (1897), 4, 268; *J. pr. ch.*, 1897, 56, 353). A solution of sodium carbonate (5), potassium iodide (10), alcohol (20), water (100), is subjected to electrolysis at 60° C. by a current density (anodic) of 1 ampère per 1 sq. dm., using a porous cell as diaphragm around the anode; the cathode may be surrounded with a cell of parchment paper and a stream of CO_2 passed through the liquid. The nascent oxygen set free at the anode liberates the iodine from the KI, which then combines with the alcohol and water to produce iodoform:—

$$C_2H_5OH + 10I + H_2O = CHI_3 + 7HI + CO_2.$$

The iodoform is hourly removed and the solution made up to its original strength by the addition of Na_2CO_3, KI, and alcohol. Iodoform is a somewhat volatile yellow solid, with a characteristic odour, largely used as an antiseptic for wounds.

Statistics.—In 1909 Germany exported 216 dz. of iodoform and bromoform. (1 dz. = 100 kilos = $\frac{1}{10}$ ton.) The United States import in 1910 was only 31 lbs.

V. THE ETHERS

Ether, Sulphuric Ether, $(C_2H_5)_2O$,

Is prepared on a very large scale by heating to boiling (140°-145° C.) in a large lead-lined vessel A a mixture of 9 parts concentrated H_2SO_4 and 5 parts 96 per cent. alcohol, while simultaneously a constant flow of alcohol into the boiling liquid takes place from a tank B through a leaden pipe dipping into the liquid. The inflowing alcohol is added at such a rate that the volume of the mixture remains unchanged and the continuous ebullition proceeds smoothly without breaks.

The following action takes place:—

(1) $\underset{\text{Alcohol.}}{C_2H_5.OH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5.H.SO_4} + \underset{\text{Water.}}{H_2O}.$

(2) $\underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5.H.SO_4} + \underset{\text{Alcohol.}}{C_2H_5OH} = \underset{\text{Ether.}}{C_2H_5—O.C_2H_5} + \underset{\text{Sulphuric acid.}}{H_2SO_4}$

Side actions simultaneously take place, producing sulphonic acids and esters (*e.g.*, $HO.CH_2.CH_2.SO_2.O.C_2H_5$) which are found in commercial ether (see *Prunier, Comp. Rend.*, 1897, **124**, 1028, 1239). The sulphuric acid, although continually regenerated, gradually becomes diluted with water and is partially destroyed by the side actions, so that after a time its efficiency ceases. 600 kg. of H_2SO_4 (sp. gr. 1.840) suffice to convert 40,000 kg. of 96 per cent. alcohol into ether in the course of a six weeks' continuous operation.

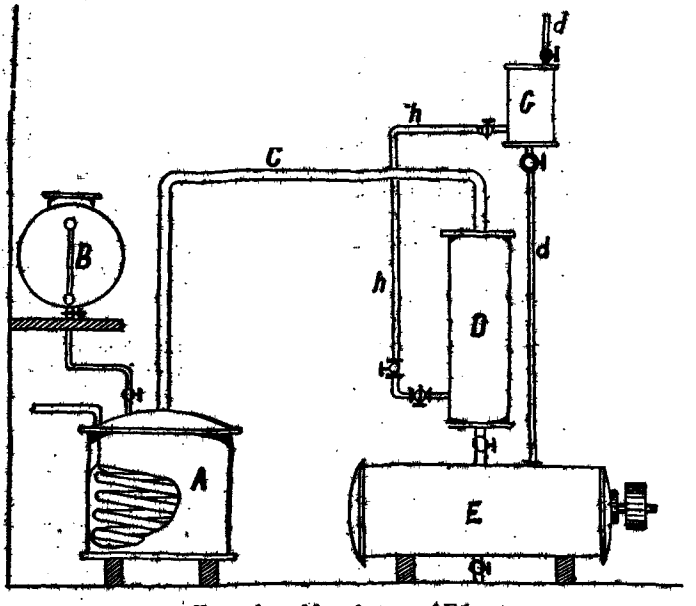


FIG. 167.—Manufacture of Ether.

Krafft and Roos (German Patent, 69,115) in their process replace the sulphuric acid by **benzene sulphonic acid** and thus avoid the formation of volatile sulphonic acids:—

(1) $C_6H_5.SO_3H + C_2H_5OH = C_6H_5.SO_3.C_2H_5 + H_2O.$

(2) $C_6H_5.SO_3.C_2H_5 + C_2H_5OH = C_6H_5.SO_3H + (C_2H_5)_2O.$

A recent proposal by Schröter and Sondag ("Ber.," 1908, 41, 1921) to replace sulphuric acid by **methionic acid**, $CH_2(SO_3H)_2$, promises to become important. If a mixture of alcohol and methionic acid is heated to 140° and a stream of alcohol allowed to flow into the liquid as described above, ether and water continually distil over while the methionic acid undergoes no change. The method is especially valuable for producing ethers of high molecular weights. For example di-iso-amylether is produced by merely heating amyl alcohol with one-tenth of its weight of methionic acid.

The ether distilling away from A passes by means of the tube C into the condenser D and runs into the tank E, where it is agitated by stirrers with milk of lime or sodium carbonate solution in order to remove any acid carried off. Permanent gases produced in the reaction (*e.g.*, ethylene) escape through the tube *dd* into the air, the condenser G returning any ether vapour to D and E by means of the tube *hh*.

The crude ether is now drawn off and separated from alcohol by rectifying in an ordinary still. It is then carefully rectified in columnar stills.

Methods of Purifying Commercial Ether.—The usual process for purifying ether consists in shaking with water (which removes alcohol) and distilling. Dr H. Timpe (German Patent, 124,230) obtains a pure water and alcohol free ether without distillation by shaking it with aqueous H_2SO_4, of 30-50 per cent. concentration, which absorbs both water and alcohol. Most of the water taken up at 18° C. may be frozen out by cooling the ether in a freezing mixture. The purest sorts of ether are obtained by treating with metallic sodium which destroys all water and alcohol, distilling, and keeping over sodium.

The laboratory method of purifying commercial ether consists in washing twice with water, keeping two days over calcium chloride, treating with sodium wire for two to three days until hydrogen ceases to be evolved, and distilling over phosphorus pentoxide. It should be kept in stout bottles with stoppers waxed in, or else over sodium wire in a bottle provided with a calcium chloride tube.

Properties.—B.P. 35° C. at 760 mm.; M.P. −113° C.; D_0 0.736; D_{15} 0.720. 100 parts ether dissolve 3 parts water; 100 parts water dissolve 10 parts ether. Vapour very inflammable and forms an explosive mixture with air. An excellent solvent for organic compounds.

Uses.—Used as a solvent and extracting agent, especially in the manufacture of celluloid, etc. etc. Also used as an anæsthetic for minor operations, since its vapour produces first intoxication and then unconsciousness.

Statistics.—The English import was: 1906, 11.57 gals.; 1910, 337 gals.; value in 1910, £286. The English export was: 1910, 334 gals. (value £156). The duty on ether is £1. 16s. 6d. the gallon (1910).

The United States in 1910 imported 337 lbs. of ether (value $66). The duty is 8 cents per lb.

Methyl Ether, $CH_3.O.CH_3$

Is prepared from methyl alcohol and sulphuric acid in exactly the same way that ordinary ether is prepared from ethyl alcohol and sulphuric acid. Colourless gas, with ethereal odour, condensing at −21° C. to a colourless liquid. 1 vol. H_2O dissolves 37 vols. of the gas, 1 vol. H_2SO_4 over 600. Used instead of ammonia in ice-producing machines.

VI. THE ESTERS (ALSO CALLED ETHERS), INCLUDING FRUIT ESSENCES.

These are produced by heating together a mixture of an alcohol and an organic acid, usually in the presence of some dehydrating agent, such as sulphuric acid, dry HCl gas, etc. The mixture is then fractionally distilled. Many esters are conveniently prepared by dissolving the organic acid in the alcohol, saturating the mixture with dry HCl gas, separating the ester as an oil by adding water, drying, and distilling.

Ethyl Formate, $H.CO.OC_2H_5$,

Is prepared by distilling a mixture of alcohol, oxalic acid (dehydrated), and glycerol. The oxalic acid splits up into formic acid and CO_2. The nascent formic acid immediately combines with the alcohol, giving the ester. Volatile liquid, B.P. 54.5° C.; used in the preparation of artificial rum and arrak.

Ethyl Acetate (Acetic Ether), $CH_3.CO.OC_2H_5$,

Is prepared on a large scale by boiling together a mixture of alcohol, acetic acid, and H_2SO_4, usually in a steam-heated copper still, provided with a rectifying column The distillate flows into a vessel provided with stirring apparatus, and is there

shed with alkali to remove H_2SO_4, then with water, dried over $CaCl_2$, and tified over calcined magnesia. It is less frequently prepared by heating dehy- ated sodium acetate with concentrated H_2SO_4 and alcohol. Ethyl acetate may be ed from alcohol by heating for thirty minutes with a reflux condenser over P_2O_5, d then distilling.

Properties and Uses.—Pleasant smelling liquid, B.P. 77.5° C.; used as a solvent in making smokeless powder, and in other industries as well. Much used as a synthetic agent in chemistry, for example in the manufacture of **antipyrine**. Also used for perfuming fruit juices, spirits, etc., and in medicine.

The English import of ethyl acetate (acetic ether) was 3,241 lbs. (value £221) in 1906; 1,501 lbs. (value, £57) in 1910. The export in 1910 was only 56 gals. (value £2). The duty on ethyl acetate is 2s. 7d. the pound (1910).

Glycerol Acetate, Acetine, $C_3H_5.(O.C_2H_3O)_3$

Is obtained by heating together glycerol and glacial acetic acid. Used as a solvent (possessing certain advantages over alcohol, etc.), for **induline** and other colouring matters employed by the calico printer as a steam colour; also employed as an adulterant of peppermint oil and other ethereal oils. Said to be employed for gelatinising and lowering the freezing point of nitroglycerine (see p. 624).

Ethyl Butyrate (Butyric Ether), $CH_3.(CH_2)_2.COOC_2H_5$

The ethyl butyrate of commerce is really a mixture of the ethyl esters of normal **butyric acid**, $CH_3.(CH_2)_2.COOH$, and of other similar acids. It is obtained: (1) by distilling rectified butyric acid with alcohol and sulphuric acid; (2) by saponifying butter with caustic soda and distilling the resulting soap with alcohol and H_2SO_4; (3) the pod of the carob bean, *Siliqua dulcis*, is chopped up, mixed with chalk mud, and allowed to ferment. The pod contains 2 per cent. **isobutyric acid**, $(CH_3)_2.CH.COOH$, and 40 per cent. sugar; this ferments to ***n*-butyric acid**, and, after some weeks, the calcium butyrate is isolated and distilled with alcohol and sulphuric acid, when the ester is produced.

The substance is used for flavouring purposes; B.P. 110°-121° C.

400 gals. (value £278) were imported into England in 1910. The export was 5 gals. (value £6). The duty on ethyl butyrate is £1. 1s. 10d. per gallon.

Amyl Butyrate, $CH_3.(CH_2)_2.COOC_5H_{11}$

Is obtained in a similar manner to ethyl butyrate, replacing, however, the alcohol by fusel oil amyl alcohol. Used in making "apricot essence."

Amyl Acetate, $CH_3.CO.O.C_5H_{11}$

Is obtained from amyl alcohol and acetic acid by heating in the presence of H_2SO_4, distilling, or by saturating the mixture with dry HCl gas, adding water, and separating the oil. Pure amyl acetate boils at 138° C. It has a pleasant "pear-like" odour, and, when mixed with ethyl acetate and alcohol (1 : 10), is sold as "**Pear Oil**" for flavouring confectionery, sweets, etc. Pure amyl acetate is used as a standard oil in photometry (Hefner Lamp). It is also used as a solvent for many technical purposes. (See pp. 49, 298, 312.)

About 450,000 gals. of amyl acetate are annually employed in the United States as a solvent for the manufacture of artificial leather, lacquer, and other industries. It is used extensively as a solvent for various nitro-celluloses. *Butyl Acetate*, produced from butyl alcohol and acetic acid, has similar solvent powers to amyl acetate (see p. 314).

Amyl-iso-valerate, $C_4H_9.CO.OC_5H_{11}$

Is obtained from amyl alcohol from fusel oil by oxidising it with potassium dichromate and H_2SO_4. 5 parts of powdered potassium dichromate are placed in

a vessel provided with a reflux condenser. 4 parts of water are added, and then mixture of 1 part of the amyl alcohol, B.P. 129°-131°, and 4 parts of concentrat H_2SO_4 allowed to run slowly in. A vigorous action ensues, owing to the formati first of **iso-valeric acid**, which then unites with amyl alcohol to produce amyl-is valerate, thus: $3C_5H_{12}O + 2O_2 = (C_5H_{11}).O.(C_5H_9O) + C_5H_{10}O_2 + 3H_2O$. When t reaction slackens the liquid is boiled until iso-amyl aldehyde (known by its su cating smell) ceases to escape through the reflux condenser. The liquid is then distilled, the distillate neutralised with sodium carbonate, when the amyl-iso-valerate separates as an oil. This is run off, dried, and rectified. Another method of producing amyl-iso-valerate is to distil a mixture of 12 parts dehydrated sodium valerate with 8 parts of amyl alcohol and 12 parts concentrated H_2SO_4.

Properties.—Oily liquid, B.P. 188°. Has a pleasant smell of apples, and consequently is sold under the name "apple-oil" for flavouring sweets, liquors, etc.

Amyl Caprionate, $CH_3.(CH_2)_8.COOC_5H_{11}$,

Is the main constituent of cocoa-nut oil essence or cognac essence, which contains as well ethyl esters of caprionic, caprylic, lauric, myristic, and palmitic acids. It is obtained from the volatile acids of cocoa-nut oil (formed by saponifying the oil, decomposing the resulting soap by H_2SO_4, and steam distilling). The volatile acids are dried, mixed with amyl alcohol, saturated with dry HCl gas, and heated. (H_2SO_4 may be used instead.) After twenty-four hours the ester is separated as an oil by adding water, agitated with Na_2CO_3 solution, washed with water and rectified.

The substance is used for flavouring **artificial cognacs.** It is very similar to **wine oil**, which is obtained by distilling wine (see p. 251).

Methyl Benzoate, $C_6H_5.CO.O.CH_3$,

Is obtained by distilling benzoic acid and methyl alcohol with H_2SO_4. Used in perfumery as **Niobe Oil.** B.P. 199.2° C. (746 mm.).

Ethyl Benzoate, $C_6H_5CO.OC_2H_5$,

Prepared by action of dry HCl gas on benzoic acid dissolved in alcohol. Separates as an oil on adding water. B.P. 213°. Used for manufacturing essences and perfumes. Also in synthetic chemistry, for introducing the benzoyl group into certain synthetic drugs, especially local anæsthetics.

Methyl Salicylate, $C_6H_4(OH).COO.CH_3$,

Is obtained in a similar manner by distilling methyl alcohol, salicylic acid, and H_2SO_4. Occurs naturally in oil of wintergreen (from *Gaultheria procumbens*). Used in perfumery and in medicine.

Methoxymethylsalicylate, $C_6H_4(OH).COO.CH_2.OCH_3$,

Used in medicine under the name "Mesotan." Manufactured by the Elberfelder Farbenfabriken (German Patent, 137,585) by heating monochlormethyl ether, $CH_2Cl.O.CH_3$ (prepared by passing HCl gas into a mixture of formaldehyde and methyl alcohol), dissolved in benzene, to 40° C. (not over) with sodium salicylate. The following action takes place:—

$$C_6H_4(OH).COONa + ClH_2.Cl.OCH_3 = NaCl + C_6H_4(OH)COO.CH_2.OCH_3.$$

The product is washed with H_2O, the benzene distilled off, and the oil distilled *in vacuo*.

Ethyl Nitrite, $C_2H_5.NO_2$,

Is obtained by mixing 3 parts crude 40 per cent. HNO_3 with 12 parts alcohol (sp. gr. 0.834-0.830) and distilling on the water bath until red fumes appear,

neutralising the distillate with calcined magnesia, and pouring off from this after twenty-four hours; 3 parts of alcohol are added and then the whole is rectified.

The substance decomposes, becoming acid on standing, when it must again be neutralised with magnesia and rectified. Ethyl nitrite boils at + 16° C.; the commercial "Ethyl Nitrite" is an alcoholic solution of the substance. Used in the manufacture of the cheaper kinds of **essences**; also in medicine.

Amyl Nitrite, $C_5H_{11}NO_2$,

Is prepared by heating pure amyl alcohol from fusel oil (B.P. 130°-131° C.) to 70°-90° C., and then passing in nitrous fumes until the smell of the amyl alcohol becomes imperceptible. The product is as rapidly as possible neutralised with calcined magnesia (or dilute sodium carbonate solution), dried over $CaCl_2$, and distilled on a water bath of boiling brine. The fraction 90°-100° C. is collected and redistilled, when the pure product, B.P. 96° C., comes over.

Amyl nitrite is a pleasant smelling liquid used in the manufacture of certain mineral waters, scents, sweets, etc., in spite of the fact that the substance is poisonous, causing headache, giddiness, and other unpleasant symptoms. It is used in the synthetic dye industry for preparing nitroso- and diazo-compounds. Also used to a small extent in medicine.

We append here the constitution of some **commercial fruit essences** (also fruit **ethers**) composed of the above-mentioned esters.

Apple Essence.—Amyl isovalerate, 100; ethyl nitrite, 50; ethyl acetate, 50; acetaldehyde, 7½; alcohol, 793 parts.

Pear Essence.—Amyl acetate, 200; ethyl nitrite, 100; ethyl acetate, 50; alcohol, 645.

Apricot Essence.—Amyl butyrate, 190; benzaldehyde, 35; alcohol, 770.

Strawberry Essence.—Amyl formate, 9; butyric acid, 9; isovaleric acid, 18; acetic acid, 27; ethyl acetate, 13; essence of violets, 9; alcohol, 915.

Cherry Essence.—Amyl acetate, 15; benzaldehyde, 10; sweet oil of oranges, 1; cassia oil, 2; lemon oil, 2; oil of cloves, 2; amyl butyrate, 8.

Peach Essence.—Amyl isovalerate, 100; amyl butyrate, 100; amyl acetate, 20; benzaldehyde, 10; alcohol, 770.

See also **Synthetic Perfumes**, p. 136.

Statistics.—The United States in 1910 imported 1,000 lbs. (value $775) of fruit ethers. Duty is $1 per lb.

SECTION XI

The Illuminating Gas Industry

THE ILLUMINATING GAS INDUSTRY

By Ernest A. Dancaster, B.Sc.

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See also under **Acetylene**, p. 401.

The illuminating gas industry originated in England with Murdoch in 1792. London streets were illuminated by gas in 1813, Paris in 1815, Berlin, 1826. The industry is to-day an enormous one. England still produces the most gas, distilling in 1909 nearly 16,000,000 tons of coal and producing 6,900 million cub. yds. of gas, representing 150 cub. yds. per head for the whole country and 292 cub. yds. for London. The introduction of Auer's incandescent mantle in 1885 opened a new epoch in the coal-gas industry, which was at one time seriously threatened by the electric light industry. More recently the introduction of carburetted water gas, either alone or more usually mixed with ordinary coal gas (say 10-20 per cent. carburetted water gas in the coal gas), represents a fresh development, since by the addition of this gas the heating and luminous value of the gas can be greatly increased, and be made independent of external disturbances.

The production of a luminous gas is now of less importance than formerly, and, indeed, with the general introduction of the incandescent mantle, may be dispensed with, the heavy luminous hydrocarbons merely serving as sources of heat (a cubic metre of coal gas should yield at least 5,000 calories). The essential modern improvement, then, consists of producing luminosity *not* by glowing carbon particles (*e.g.*, the cause of the luminosity of the candle, oil, and ordinary gas flame), but by the more efficient glowing incandescent mantle.

COAL GAS

General.—Coal when heated in a closed space in absence of air undergoes destructive distillation, with the production of a residue of (*a*) **coke**, (*b*) tar, (*c*) aqueous fluid, and (*d*) gas.

Besides coal, we find wood, peat, bituminous shales, brown coal, bones, certain oils, and residues left in the manufacture of beet sugar subjected to destructive distillation on the industrial scale with the object of obtaining valuable chemical products.

Coal is subjected to destructive distillation (*a*) in gasworks, (*b*) in coke ovens, but with very different objects.

In **gasworks** the main object is to produce **gas** for illuminating purposes, and the other products—such as coke, ammonia and tar—are by-products. In **coke ovens**, however, the main object is to produce **coke** for metallurgical operations, the gas, tar, and ammonia being here by-products. In gasworks the coal is heated in small closed earthenware retorts, whereas in coke ovens the coal is de-gassed in large fire-brick chambers.

In Germany the coke ovens are greatly developed, over two-thirds of the total yield of tar and benzol being obtained from this source, together with very large amounts of illuminating gas. In England and the United States, however, coke ovens are but slightly developed, almost all the illuminating coal gas being obtained from gasworks. See p. 392.

For the economical production of coal gas a special sort of coal—the so-called gas coal—must be used, which yields a large amount of gas of good calorific power.

Gas coal usually contains 4-5½ per cent. H and 5-16 per cent. O, but a mere chemical analysis yields little information as regards the gas value of a coal; different coals—even when analysing the same—often behave quite differently, and the suitability of a coal for gas production is best ascertained by actual trial on a large scale. In general 1 kg. of good gas coal (calorific value =7,500 calories) should yield 300-350 l. of gas (calorific value, 1,500-1,850 calories) representing 20-25 per cent. of the heating value of the coal. 100 kg. of good gas coal should yield 16-19 kg. gas=30-35 cub. m., 65-68 kg. coke, 5 kg. tar, 8 kg. ammoniacal water, and 3 kg. loss. Coal on storage undergoes rapid deterioration, a continual loss of gas taking place, as well as surface oxidation.

Manufacture of Coal Gas in Gasworks

The Retorts.—In gasworks coal gas is always prepared by the destructive distillation of coal in small closed fire-clay retorts, externally heated to from 950°-1,400° C.

Horizontal Retorts.—The most common form is of D-shaped cross section, but oval and circular retorts are also known. They are usually set horizontally in beds of from three to twelve, heated by the same furnace. The walls of the ovens support the ends of the retorts, and a number of transverse partitions built in the ovens support them at intervals along their length. In large works these retorts are usually about 20 ft. long, and are fitted with an iron mouthpiece and self-sealing lid at each end. In small works shorter retorts, which are closed at one end, are used.

A, Fig. 170, shows the retorts in cross section, and Fig. 168 represents a longitudinal section through the furnace.

The heating is now invariably done by gas firing in regenerative furnaces, the heat of the burnt gases being utilised in heating that of the entering air. By this means an enormous saving in the amount of coke used for firing has been effected—the old coke fires required for every 100 tons of coal distilled about 30-40 tons of coke burnt, against 12-15 tons now required. Consequently at the present time at least 80 per cent. of the produced coke is available for selling. Moreover since gas fires give a much greater heat (1,400° C. in the hottest part), a large yield of gas is simultaneously obtained.

The firing gas, principally CO, passes into C (Fig. 168) from the gas-generator B, and is here mixed with a stream of pre-heated air, and burns, encircling the retorts as it does so on every side; the hot burnt gases pass away through a system of brickwork channels, running parallel to which is a similar and separate system of channels conveying the entering air, which is thereby intensely heated before it enters the gas chamber. The exhausted gases finally pass away through D. Immediately under the generator B is a water-tank over the surface of which the entering air passes, so that it enters B charged with moisture, which has the double effect of cooling the gas-producer, thereby prolonging its life, and of producing a little water gas. The gas generated

in the retorts passes away up the tubes *gg*. Usually the gas is sucked out of the retorts by the exhauster (p. 393), so that the gas inside is at a pressure slightly less than atmospheric pressure (the pressure must not be too low or air is sucked in). This is done in order to withdraw the heavy hydrocarbon gases as rapidly as possible from the heat, in order that they may not be decomposed. Nevertheless much gaseous decomposition occurs, and in consequence the inner walls of the retort become lined with "retort carbon." Much of this carbon goes over as a fine dust with the gases into the hydraulic main.

At the close of the operation, when all the gas has distilled over, the lid of the retort is loosened, the issuing gas carefully ignited, and the gas remaining in the retort allowed to burn quietly away. The coke is then raked out and rapidly quenched with water. The retorts are recharged as soon as possible after the withdrawal of the coke. The charging is often done by hand by means of long shovels ("scoop-chargers"), worked by three men. In larger installations, however, a mechanical charger is used, usually consisting of a travelling trolley running on rails up and down in front of the retorts and fitted with a "scoop-charger" and coal hopper.

In West's manual charging machine, worked by two men, there is a double scoop which is fed with coal from the hopper. When full the scoops are pushed into the retorts by a rod and reversed by means of a handle attached to the rod. The charger is then withdrawn. An apparatus for breaking up coal is also provided, with an elevator for transferring the broken coal to a hopper which supplies the hoppers of the chargers as required. A mechanical drawing apparatus is also used. This consists of a rake which is manipulated by means of a bar held in channel guides.

Modern machine stokers, *e.g.* Fiddes-Aldridge, charge and recharge at one stroke.

The retorts last for 1-3 years, being kept during the whole of that time at a bright red heat.

Inclined retorts set at an angle of 30°-36° have come into use during recent years. These are usually about 15 ft. long, and of D-shaped cross section. The coal is poured into the retorts from a hopper, and the coke is withdrawn by opening the door at the lower end, when it falls out of itself, thus greatly diminishing the manual labour of charging and discharging.

Vertical retorts have been tried, but until recently with little success. Now, however, there are on the market vertical retorts which are far superior to the horizontal retorts above described. It was formerly thought that the coal would swell up and prevent the gas escaping freely, so that the resulting gas would be largely decomposed, and be poor in heavy hydrocarbons. Trial, however, has shown that the exact reverse holds true, the gas being of excellent quality on account of the fact that the inner core of coal remains relatively cool almost to the last, and the gas, escaping rapidly through this core, comes out rich in heavy hydrocarbons. The coke produced is denser and harder than that of horizontal retorts, the tar much thinner, and the yield of ammonia 50 per cent. greater, while that of the cyanides is smaller. Moreover, much less space is taken up by the retorts, and charging and discharging are especially easy—the retorts being made slightly larger at the base, so that the coke readily falls out, while the charging occurs by means of overhead hoppers.

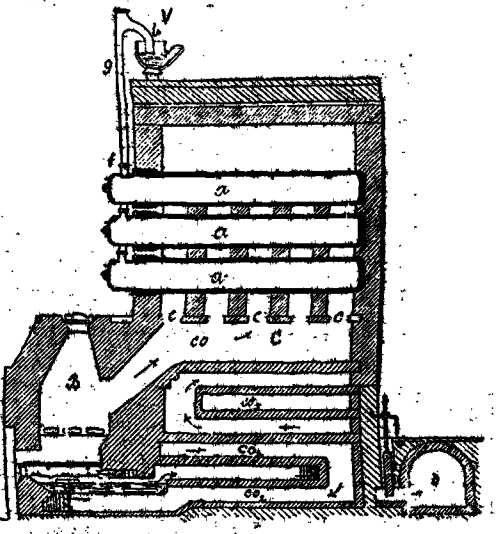


FIG. 168.—Longitudinal Section of Gas Retort Furnace.

Fig. 169 shows a vertical cross section of the new vertical retorts of Dr Bueb's system as erected by the Dessauer Gas Anstalt. R are the retorts, ten retorts in two rows, or eighteen retorts in three rows usually going to a furnace. G is the gas generator, which is fed with coke through *ef*. The producer gas, mixed with air, circulates as a very hot flame around the retorts in the flues *n*, the hot-burnt gases passing out through the regenerators *m*, where it gives up its heat to the entering air, and finally escapes through the smoke-flue *r*. The retorts are charged with coal by the hopper *a*, and the coke withdrawn below, being discharged through *c* into a trench *d*. The gas escapes through the hydraulic main V into the gas-main H, while the tar runs away by *k*.

Continuous carbonisers, such as *Woodall-Duckham* and *Glover-West*, have also been tried, and have proved very successful. Also **coking chambers**—similar to coke ovens—consisting of horizontal or inclined chambers, 2-3 m. high, and of a considerable length, holding 10-15 tons of coal, with a period of distillation of twenty-four hours (also continuous working ones), have been tried, and are fairly satisfactory.

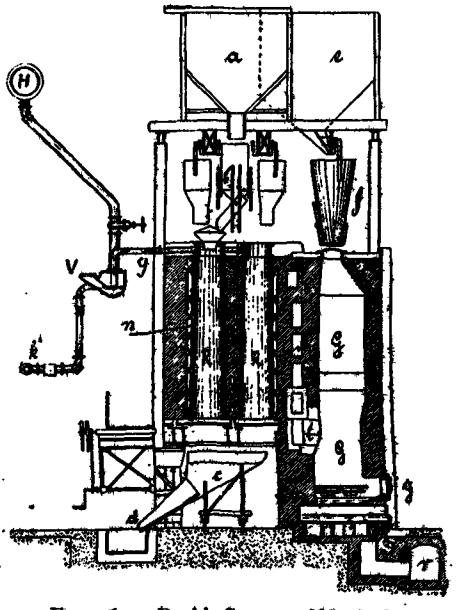


FIG. 169.—Bueb's System of Vertical Gas Retorts.

Course of the Distillation.—A temperature of about 1,000° C. is required for the de-gassing of coal; formerly a temperature of 960° C. was deemed sufficient, but now it is common to go up to 1,200°-1,400° C., and coal which has been heated to 1,500° C. still retains some H, N, and O. In general, the higher the temperature and the longer the period of heating the larger the volume of gas produced. The gas which comes off first at the lower temperatures is rich in heavy hydrocarbons and possesses much illuminating and heating power. The last portion of gas, obtained at the highest temperature, consists principally of hydrogen, and is of poor illuminating power. In other words, the lower the temperature of production the better the quality of gas but the smaller the quantity. A large volume of gas is invariably produced at the expense of its quality.

The following table shows this, the numbers referring to the volume of gas produced by distilling 100 kilos of English gas coal at various temperatures:—

Temperature of Distillation.	Volume of Gas Produced in Cubic Metres.	Candle-Power of Gas.
1. Dark red heat, 800°-1,000° C. - - -	23.4	20.5
2. Bright red heat, 1,000°-1,100° C. - - -	27.5	17.8
3. White heat, 1,200°-1,400° C. - - -	34.0	15.6

The coal undergoes a loss of weight of 17-18 per cent. The following numbers show the variation in the composition of the gas evolved in successive stages of the distillation, the gas being collected in three successive lots of equal volumes:—

Stage of Distillation.	H.	CH_4.	CO.	Heavy Hydrocarbons.	CO_2.	Residue.
	Per Cent. (Vol.)	Per Cent. (Vol.)	Per Cent. (Vol.)	Per Cent. (Vol.)	Per Cent. (Vol.)	Per Cent. (Vol.)
1. First gas evolved -	28.3	46.6	9.4	9.4	4.0	2.3
2. Intermediate gas -	49.0	31.7	8.1	4.3	2.0	4.9
3. Last gas - -	55.3	27.2	8.8	1.7	1.8	5.2

The various portions of gas when mixed together analysed as H=45.2 per cent., CH_4=35 per cent., CO=8.6 per cent., heavy hydrocarbons=4.4 per cent., and residue=4.8 per cent.—all by volume. The original coal analysed as C=77.2 per cent., H=5 per cent., O+N=9.3 per cent., H_2O=2 per cent., ash=6.5 per cent., and yielded 17.7 per cent. by weight of gas=30.2 cub. m. per 100 kilos.

The N contained in the coal passes over partly as NH_3, partly as free N, a small fraction escaping as HCN, pyridine, quinoline, etc. The S (usually 0.5-1 per cent., sometimes 2 per cent.) escapes principally as H_2S and CS_2, but part remains behind in the coke.

Purification of the Crude Gas.—The gas coming from the retorts is very impure, containing tar, moisture, ammonia, sulphuretted hydrogen, hydrocyanic acid, naphthalene, etc., from which it must be freed before use.

The crude gas passes out of the retorts by the *ascension pipes g g* (Figs. 168 and 170), which lead it into the *hydraulic main* v (Fig. 170, shown in section in Figs. 168 and 169), where the bulk of the tar and moisture condense. The hydraulic main usually runs along the top of the retort bench, and the dip pipes which enter it are sealed by the liquid in the bottom of the main. This liquid consists of a layer of tar above which is a layer of ammoniacal liquor, both layers being deposited by the gas which has previously passed through. The tar and ammoniacal liquor are drawn off by a pipe so as to keep a constant level of both liquids. The hydraulic main is often divided into several sections, each of which is provided with an outlet pipe passing into a large main F (Fig. 170) known as the *foul main*. The water seal in the hydraulic main is sometimes replaced by mechanical devices known as anti-dips.

The gas is partly freed from ammonia, carbon dioxide, hydrogen sulphide, and

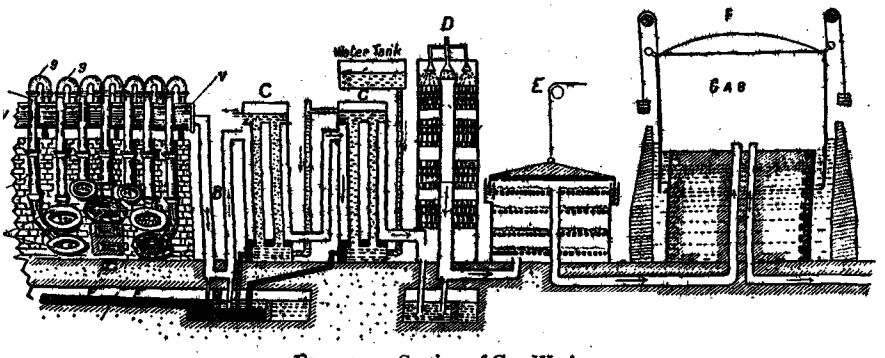


FIG. 170.—Section of Gas Works.

cyanogen by the liquor in the hydraulic main. It now passes into the air-condensers B (Fig. 170) where it is further freed from a quantity of tarry matter by deposition. In some works vertical condensers are used, but often the pipes, which are from 50-80 ft. long, are arranged in nearly horizontal rows which are exposed to the air. They are connected to a second row which passes underneath the first and so on; frequently there are about a dozen of these rows of pipes, one beneath the other, and cooled in summer by dripping water. Then the gas (especially in Continental works) is subjected to water cooling in C C, which is specially useful in hot weather.

Even after a very thorough cooling a portion of the tar remains suspended in the gas in the form of fine drops. Consequently in many works the gas passes into a "tar extractor," where it is made to pass through a series of perforated iron plates. Fig. 171 shows Pelouze's form, consisting of a hanging bell *a* suspended in water and made up of three layers of finely slit iron plates. The fine tarry drops in the gas condense to larger drops in passing through the slits, and so are separated. A regulator F raises or sinks the bell, and so regulates the rate at which the gas passes. Some ammoniacal liquid and practically all the tar is separated by this device.

Either before or after the tar extractor is placed the *exhauster*. This is really a pump used to draw the gas from the retorts and condensers and to force it through the washing and purifying apparatus. Sometimes fans or blowers are used for this purpose, when the gas has to be driven a considerable distance through small mains.

The gas now enters the *water scrubbers* D (Fig. 170). In some of the older works these take the form of tall towers packed with coke or wooden checker-work, down which water or weak liquor from the hydraulic main and condensers mixed with the washings from the last stage of the washing process is caused to trickle. Two at least of these scrubbers are used in series. More usually, however, some form of *washer scrubber* is used in which the gas is passed in fine streams through water or dilute liquor. Such scrubbers are far more efficient and occupy much less room.

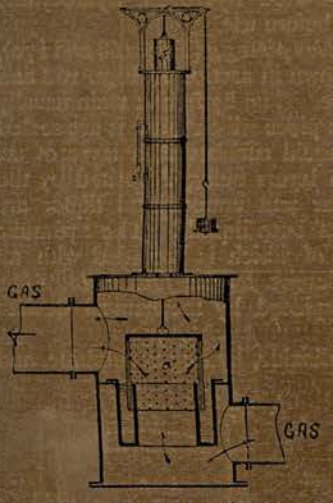


FIG. 171.—Pelouze's Tar Extractor.

In the "Standard" washer scrubber (Fig. 172) bundles of iron, or a combination of wood and iron B B, attached to a horizontal shaft F are slowly revolved, and thoroughly wetted by passing through water or weak liquor placed in the bottom of the washer. The gas is caused to pass through the wet bundles. The liquor passes through the apparatus in the opposite direction to the gas so that as the latter becomes more pure it meets a stronger solvent. Two such scrubbers in series are used, the first being fed with dilute liquor and the second with water. In the most modern form of this scrubber the bundles are made entirely of wood. The "New" washer scrubber has discs covered with bundles of Brazilian bass (*piaçaba*) fibre which press against the faces of the sections of the scrubber and the gas passes between the wet fibres. Between each pair of scrubbing chambers there is a still chamber.

In many works the gas before passing into the water scrubbers is passed through a scrubber half filled with tar oils of B.P. 250°-300° C. in order to extract the final residues of solid naphthalene, $C_{10}H_8$.

Although most of the naphthalene is condensed with the tar, yet some passes on as a vapour in the gas (1 cub. m. gas at 30° C. can hold 1 g. $C_{10}H_8$ at 0° C., 0.15 g.) and can lead to stopping up of the smaller section gas pipes. These tar oils take up over 16 per cent. naphthalene and are

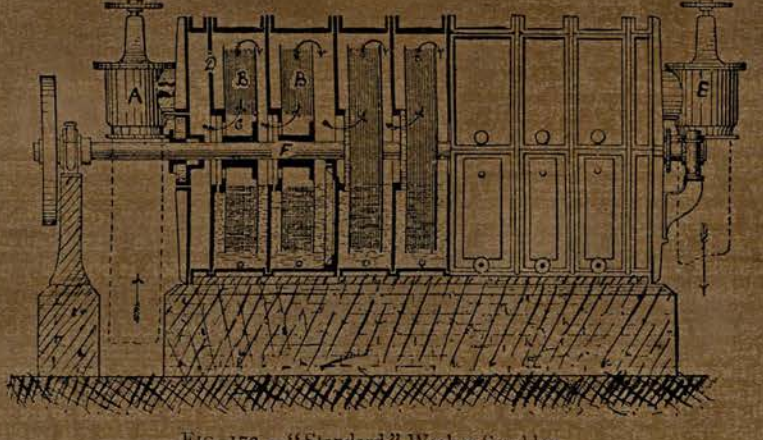


FIG. 172.—"Standard" Washer Scrubber.

then run off into the tar well. Since the tar oils could also extract benzol from the passing gas, they are charged with about 3 per cent. benzol to start with.

In the scrubbers practically all the ammonia, much CO_2, and some H_2S and HCN are removed. The resulting ammoniacal-gas water contains about 2 per cent. NH_3. The gas, however, still contains volatile sulphur compounds (princi-

pally H_2S with a little CS_2, HCN, and CO_2. To remove these the gas now passes through a series of *purifiers*, E (Fig. 170). These are usually rectangular iron vessels, the dimensions of which vary according to the amount of gas for which they are intended. The sides of the lid dip into a water seal. Inside these vessels are placed horizontal wooden (sometimes cast-iron) grids, placed one above the other. The purifying material is spread on these to a thickness of about 8 in. The gas enters the purifiers at the bottom and passes out at the top. In some Continental works a different method has been recently introduced in which the horizontal grids are replaced by composite grids which are so arranged as to cause the gas to traverse the purifying material chiefly in a horizontal direction.

A complete set of purifiers consists of eight vessels arranged in four pairs. As usually arranged the first pair are charged with slaked lime, the next two with hydrated ferric oxide mixed with sawdust or wood chips, and the third pair with sulphided lime (hydrated lime through which gas containing H_2S but no CO_2 has been passed). The last pair act as check vessels and contain lime and ferric oxide, or Weldon mud. Sometimes the iron oxide in the second pair of purifiers is replaced by Weldon mud which is essentially a hydrated manganese oxide and acts in the same manner as the ferric oxide. In this case the arrangement of the purifiers is sometimes altered, the second pair containing the sulphided lime and the third pair containing Weldon mud. The first pair always contains slaked lime.

At first the CO_2 and H_2S in the gas are absorbed by the lime in the first purifiers, but as the free lime gets used up the H_2S is liberated by further quantities of CO_2, so that ultimately all the H_2S passes on into the second pair of purifiers where it is absorbed by the moist ferric oxide (or Weldon mud), with the formation of iron (or manganese) sulphide. The gas then passes into the third pair of purifiers where the CS_2 is absorbed by the sulphided lime. It then passes through the last pair which remove any remaining traces of H_2S, and finally passes to the gas holder.

Frequently the sulphided lime vessels are left out, and sometimes the purification of the gas after leaving the washer scrubbers is limited to passage through hydrated ferric oxide only or through slaked lime alone.

This dry purification is not very perfect, since traces of sulphur (0.5-0.6 g. per cub. m.) and HCN still remain.

The chemical actions which take place are very various and complex. The slaked lime takes up CO_2: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$). It also takes up H_2S, forming $Ca(SH)_2$, which then reacts with any CS_2 forming the sulpho-carbonate, $CaCS_3$. CO_2 gradually decomposes the $Ca(SH)_2$, thus: $CO_2 + Ca(SH)_2 + H_2O = CaCO_3 + 2H_2S$. Moist iron oxide unites with the H_2S, thus: $2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O$, and the iron sulphide may be regenerated either by exposing to air in heaps, or by mixing a little air (1-1.5 per cent.) with the gas passing through the generator, when S is set free: $Fe_2S_3 + 3O = Fe_2O_3 + 3S$, and further H_2S is simultaneously oxidised in the presence of the moist iron hydroxide: $H_2S + O = H_2O + S$, which here acts as a catalytic agent. When the iron hydroxide contains 40-50 per cent. free sulphur it becomes useless for purifying and is removed.

Hydrocyanic acid, HCN, does not unite with the $Fe(OH)_3$ but with the iron sulphide, forming Prussian blue, $Fe_7(CN)_{18}$. A part, however, unites with the NH_3 and H_2S to form $NH_4S.CN$, ammonium sulphocyanide. Where it is important to remove all HCN, the gas is (previous to passing into the purifiers) passed through a 20-25 per cent. solution of $FeSO_4 + NH_3$ contained in a standard scrubber, when the insoluble ammonium ferrocyanide, $(NH_4)_2Fe_2.Fe(CN)_6$, is deposited, and one-third of the ammonia is fixed as ammonium sulphate: $FeSO_4 + H_2S + NH_3 = FeS + (NH_4)_2SO_4$.

E. V. Evans has shown (see *J. Soc. Chem. Ind.*, 1915, 34, 9) that CS_2 can be completely removed from gas by passing it over a catalytic nickel.

Carburetted Coal Gas.—The luminosity of coal gas is sometimes increased by the addition of the vapour of very volatile hydrocarbons. This process is usually known as carburetting. The most common oil used for this purpose is "carburine" or light petroleum oil, but petroleum spirit is sometimes used, and also benzol.

The carburine is placed in a steel tank which is sunk in the ground. It is pumped as required from this tank to the evaporator which contains a number of tubes heated externally by means of steam. The carburine passes through these tubes and in doing so becomes vaporised. The vapour then passes on through a regulating valve and an injector into the gas main. The amount of vapour added to the gas is controlled by the regulating valve.

The following analyses show the difference effected in the composition of the gas by the purifying process:—

	Impure Gas from Retorts.	Purified Gas.
	Vol. per Cent.	Vol. per Cent.
H	46	49
CH_4	32	34
CO	8	8
Heavy hydrocarbons, C_2H_6, C_6H_6, etc.	4	4
NH_3	1	...
H_2S	1	trace
CO_2	4	1
Free N	4	4
	100	100

Mixed Coal Gas.—Of rapidly increasing importance (and which may in the near future lead to a great change in the whole gas industry) is the practice of adding carburetted water gas (see below, next section) to the extent of 10-20 per cent. to the coal gas. By this means the illuminating and heating power of the gas may be increased to almost any desired extent, while the gas company is rendered largely independent of the changing seasonal demand for gas, and of the partial failure of the coal-gas supply by an unforeseen accident.

The following analysis shows the composition of a purified coal gas mixed with 20 per cent. carburetted water gas:—

	H	CH_4	CO	Heavy Hydrocarbons, C_2H_4, C_6H_6	NH_3	H_2S	CO_2	N
Per cent. vol. =	50	27	14	4	...	...	1	4

Storage of the Gas is effected in large gas-holders (F, Fig. 170), "gasometers," of capacity 10,000-200,000 cub. m.—the largest in the world being in New York (500,000 cub. m.), which swim in deep water channels. The gas is distributed by means of a network of pipes, the main gas pipe being best of tarred cast iron, and 1 yd. in diameter. Through leakage in the distribution often 5 per cent. of gas is lost, though great improvements in this respect are now made. Usually 25 per cent. of the cost of the gas is due to the cost of the distributing pipes.

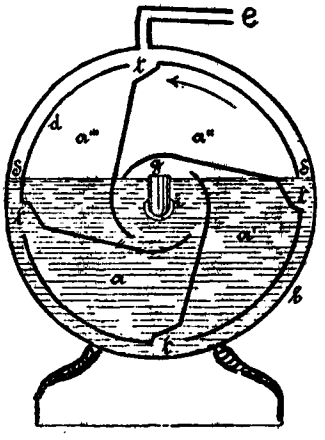


FIG. 173.—Gas Meter (Section).

The quantity of gas used is measured by means of a "gas meter," which usually consists of a vessel *b*, half filled with water (or better, glycerol water to prevent freezing in winter time), and in which a drum rotates, which is divided into four compartments, *a*, *a'*, *a''*, *a'''*, as shown in Fig. 173. The gas enters the drum at *g*, and escapes through *t* and *e*. As the gas gradually enters at *g*, it forces the drum to rotate in the direction of the arrow, and the motion being communicated by means of the axle on which the inner drum rotates to a clock-work arrangement, gives the amount of gas which has passed through. The level of the liquid in the gasometer must be kept the same (by the addition of water) if the readings are to remain the same. Dry gas meters are also in use, consisting of two leather bags, one of which fills as the other empties; also automatic meters, a penny slipped in causing the delivery of a certain fixed volume of gas.

The pressure of the gas in the gasometer usually amounts to 70-80 mm., and passes out at the burners at a pressure of 25-30 mm., although now higher pressures than this are being used.

Gas Leakage.—As small an amount as 0.02 per cent. volume of gas can be detected by its smell, which is due to traces of organic N and S compounds. When gas filters up through earth it sometimes loses all smell, and is then detected by palladium chloride paper, which turns black owing to the precipitating of metallic Pd by the CO. Long breathing of air containing only 2 per

cent. of coal gas (=0.1-0.2 volume per cent. of CO), causes poisoning. 1 volume gas + 6 volumes air is a maximum explosive mixture. Mixtures of *less* than 5 per cent. gas or *more* than 30 per cent. are non-explosive.

CARBURETTED WATER GAS

Water gas is the general name for the mixture of gases obtained by the decomposition of steam by means of incandescent carbon. In practice either anthracite or coke is used, and the gases consist of a mixture of hydrogen, carbon monoxide, and carbon dioxide. The reaction is endothermic, so that heat must be applied or the incandescent carbon soon becomes cooled, when the reaction ceases.

The mixture of gas burns with an intensely hot flame which is non-luminous. When it is to be used for illuminating purposes it must, therefore, be enriched by adding volatile hydrocarbons obtained by "cracking" or heating to a high temperature crude petroleum products, which burn with a highly luminous flame. A second reason for adding these hydrocarbons is to render the gas odorous, for the mixture is very poisonous, and being without smell it is highly dangerous unless thus mixed with some gas whose powerful odour renders it easy of detection. This mixture is known as carburetted water gas.

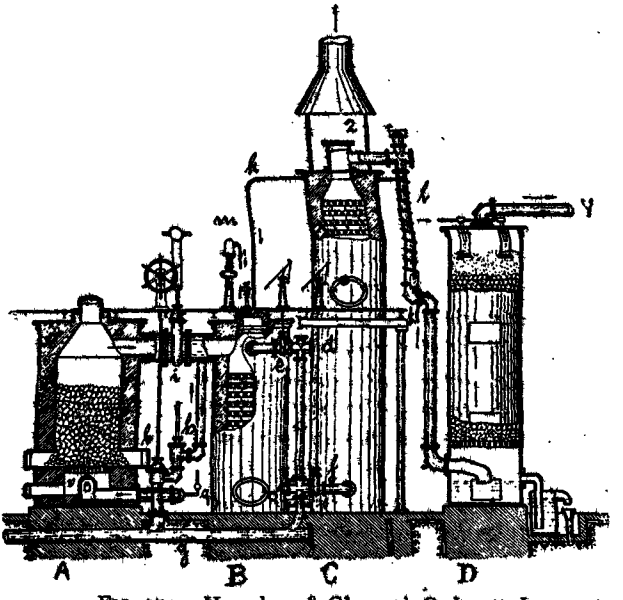


FIG. 174.—Humphrey & Glasgow's Carburetted Water Gas Plant.

It is usual to prepare the volatile hydrocarbons (oil gas) and the water gas simultaneously in the same plant. The gases are mixed as soon as formed, and are then generally submitted to a high temperature in order to prevent the subsequent deposition of the hydro-carbons, which before this final heating are not strictly permanent gases.

The forms of plant for the manufacture of carburetted water gas are very numerous and variable. They may, however, be broadly classed under two heads: (1) The continuous system, in which steam is passed uninterruptedly into a chamber containing the anthracite or coke, which is maintained at the requisite temperature by external furnaces. This system secures a continuous supply of gas but is not economical, as a considerable portion of the heat is lost in passing through the walls of the chamber. It is very little used. (2) The intermittent system, in which steam and air are alternately blown into a mass of incandescent fuel, usually in opposite directions. The steam is decomposed by the hot carbon with consequent cooling of the mass, which is then raised to the required temperature by means of the air blast. All the common forms of plant at present in use belong to this system. They are all arranged so as to secure the production and maintenance of a sufficiently high temperature (about 1,000° C.) in the generator, the presence of a sufficient depth of fuel, and a means of regulating the supply of steam and air.

Fig. 174 shows Humphrey & Glasgow's apparatus. The generator A is a steel shell lined with firebricks. It is charged with anthracite or coke which is ignited and submitted to an air-blast, which is forced in through the tube *g* and enters at *v*. Part of the fuel burns to CO_2, which, passing up through the hot coke, burns to producer gas ($CO_2 + C = 2CO$). This passes away

through *i* and enters the *carburettor* B, passes down this and then enters the *superheater* C at the bottom by means of the tube *p*. Both carburettor and superheater are steel shells lined with fire-brick and filled with brick checker-work; simultaneously with the entrance of the gas into them a stream of air from *g* is blown in through the side tubes *h*, *f*, *d*, *e*, causing the CO to burn and thus heat the brickwork in B and C to a red heat; the gas then passes out of the furnace through the opened stack valve Z, escaping into the air as CO_2. In the Lowe process, as practised in the U.S.A., the production of CO and the subsequent blowing in of air into B and C to burn it is avoided by blowing air very rapidly through the producer A, so that a sufficiency of oxygen is present all the time, and only very hot CO_2 passes away into B and C and heats them to the required temperature. When the proper temperature of the different parts of the apparatus is obtained the air blasts are shut off, beginning with that of the superheater C, and the stack valve Z is closed. Steam is then blown into the generator A through the tube *q*, and is decomposed by the hot carbon in A according to the equation $H_2O + C = CO + H_2$. It then passes into the carburettor as water gas. At the same moment the oil is introduced into the carburettor B, being pumped in through the tube *k*, and falling on the red-hot bricks in B is gasified, its vapours mingling with the water gas and passing on to the superheater C, where the oil vapours are permanently gasified, and thence through *l* (where the incoming oil is preheated by the hot gas) into the washer D (consisting of a tower filled with coke down which water trickles), where it is washed and cooled, finally passing away at Y to the purifiers and the gas-holder. When the temperature of the mass of coke becomes too low the steam is shut off, the stack valve Z opened, and the air-blast readmitted.

The gas thus prepared contains rather less than 3 per cent. of carbon dioxide, and about 0.2 per cent. of sulphuretted hydrogen. It is practically free from ammonia and the other impurities commonly found in coal gas. The purification of the gas is, therefore, a comparatively simple matter: it is simply washed and passed through two "lime" and two "ferric oxide" purifiers in series. Sometimes a fifth purifier is added as a check to ensure the complete removal of carbon dioxide and sulphuretted hydrogen. The purifiers are similar to those used in coal-gas purification, but those containing the lime must be large on account of the high percentage of carbon dioxide present in the gas.

Since water gas (without the admixture of oil gas) possesses a calorific value of 2,500 calories per cubic metre, and pure oil gas one of 8,600 calories, it is clear that by gasifying a suitable amount of oil it is easy to obtain a gas of calorific value = 5,000 K and of 16 candle-power illuminating power, and even of 20-25 candle-power (with more oil). Hence the addition of only 10-20 per cent. of this rich carburetted water gas to a poor coal gas very essentially improves it (see pp. 389, 396).

Very often "Cold Carburetting" is resorted to in Germany, the agent being benzol (C_6H_6, B.P. 81°, which at 10° C. can exist as vapour to the extent of 200 g. per cubic metre in water gas, corresponding to 6 per cent. by volume), and the carburetting is effected merely by leading the water gas through a tower down which a rain of warm benzol is falling.

OIL GAS

Just as coal gas is prepared by the destructive distillation of bituminous coal, so oil gas is prepared by the destructive distillation of mineral oil. Several processes are in use for the manufacture of this gas, by far the most important of which is the "**Pintsch**" **process**. The gas is formed by the vaporisation of mineral oil. The most important oils used for this purpose are "Mineral seal" oil, Scotch shale oil, and Russian "Solar" oil.

The manufacture of oil gas on the *Pintsch* system is carried out in gasworks somewhat similar to those used for the production of coal gas, but on a smaller scale. The main building is usually divided into three divisions, the *retort chamber*, the *purifying chamber*, and the *engine-room*. The gas-holder is placed at one end of the building, and the high-pressure storeholders at the other.

Fig. 175 shows a typical Pintsch oil gasworks. The oil is placed in a large tank sunk in the ground outside the building, from which it is pumped as required into a small cistern placed over the retort bench. A pipe leading from the cistern conveys the oil to the back ends of the upper retorts, the rate of flow being controlled by means of suitable valves. These retorts, which may be of cast iron or fireclay, and which are of Ω-shaped section, are set horizontally in pairs one above the other

and connected by cast-iron mouthpieces at one end. They are heated by means of the firebrick furnaces A. The upper retorts contain sheet-iron trays, which are sometimes filled with coke, along which the oil flows to the front of the retorts, whence it descends through pipes to the lower retorts. The oil, which has now become changed into a thick yellow vapour, passes from the back of the lower retorts down the descension pipes into the *hydraulic main*, and thence through the *condensers* B, which are usually plain vertical iron cylinders, and the *washer* C, into the *purifiers* D. The latter are somewhat similar to those used in coal gasworks: the lower portion contains water, above which are wicker trays (usually three in number), covered by a layer of about 2 in. in depth of lime, or a mixture of lime and sawdust. The gas is caused to pass through the water and over the lime and thence through the meter E into the gas-holder F. It is finally pumped from this holder by means of the compressing engines G into the high-pressure storeholders H, where it is kept at a pressure of 10 atmospheres for a short time in order to enable some of the heavier hydrocarbons to settle out as a liquid at the bottom of the holders, after which it is ready for use. The tarry matter deposited in the hydraulic main, condensers, etc., is conveyed by means of pipes into the tar tank J, the quantity of tar thus obtained being usually about 5 to 6 gals. per 1,000 cub. ft. of gas.

Pope's system of making oil gas is very similar to the above, but the oil is passed in a fine spray into the lower retort whence the vapours pass into the upper one for fixing. There are no trays in either retort.

Keith's system is designed to give a large volume of gas, though at the expense of the quality. In order to effect this the retorts are flattened towards the middle of their length, thus promoting the contact of the oil vapours with the hot surfaces of the retort at this part.

In *Tatham's* process about 15 per cent. of oxygen is added to the oil gas in order to increase the candle-power.

Oil gas consists of a mixture of CH_4, C_2H_4, C_2H_2, C_6H_6, etc., possessing a very high illuminating and heating power; but it will only burn smokeless from burners with very narrow slit orifices. Since oil gas can be easily prepared in small plants and requires only a very simple purification, it was formerly much used for lighting factories or houses remote from gasworks, but has now been displaced by electric light. The principal users are the railway companies, who deliver it compressed to 10 atmospheres at the stations, and it is stored in the iron holders under the railway carr ages under 6-8 atmospheres pressure. Until recently acetylene gas (25 per cent.) was mixed with it to improve its illuminating power, but now pure oil gas is again used, being burnt in special inverted incandescent mantle gas-burners, giving cheaper light than electric light.

The great advantage of oil gas over coal gas is its power of retaining a large portion of its luminosity when compressed. Both gases under these conditions deposit liquid hydrocarbons, but whilst coal gas loses nearly the whole of its illuminating power oil gas only loses a comparatively small portion. It is therefore particularly suitable for use wherever it is necessary or desirable to store the gas under pressure, as in railway carriages, steamboats, lighthouses, and buoys.

AIR GAS.

Air gas is the most serious rival with which acetylene has so far had to compete. It is economical, safe, and clean, the light is excellent, at least when used with incandescent mantles, and there is no troublesome by-product to be got rid of. It consists of a mixture of air and the vapour of some volatile hydrocarbon, usually petrol or carburine, but sometimes benzol. The mixture may contain too little hydrocarbon to form an explosive mixture or too much, *i.e.*, it must either contain not more than 2 per cent. or not less than 7 per cent. of petrol vapour. In the first case the gas is always used with mantles as it burns with a non-luminous flame, in the second it may be so used but is usually burnt in self-luminous burners. The plant for the production of this gas is very simple. There are several types, differing in detail and more or less in efficiency and safety.

A good type is that supplied by the Non-Explosive Gas Company.

A small hot-air engine M heated by a Bunsen burner, which burns the air gas itself, drives a

Root's blower L and thus forces a current of air through the carburettor F, where it mixes with the hydrocarbon vapour. The hydrocarbon is placed in a tank Z beneath the carburettor. Inside this tank is a horizontal axle bearing six—or in the most modern forms twelve—arms, each of which carries a tipping bucket C which empties the hydrocarbon into a feed pipe E leading into the carburettor F. The latter is a large pipe about 3 in. in diameter, inside which are overlapping ledges. The petrol vapour flows over these, and, owing to the large surface exposed, quickly volatilises. The air gas passes from the carburettor F, up the tube P, through a meter K, into the holder, which is of iron and is always of small size—about 18 in. high and 16 in. in diameter for plants supplying less than a hundred lights. The axle of the drum of the meter is extended through the front and is coupled up with the axle carrying the tipping buckets in the petrol tank, so that the rate at which the latter revolves, and therefore the rate at which the hydrocarbon is supplied to the carburettor, is regulated by the rate at which the drum of the meter is turning, which in its turn depends upon the rate at which air passes through the carburettor, and the resulting gas passes through the meter. By this means the percentage of hydrocarbon vapour is kept constant.

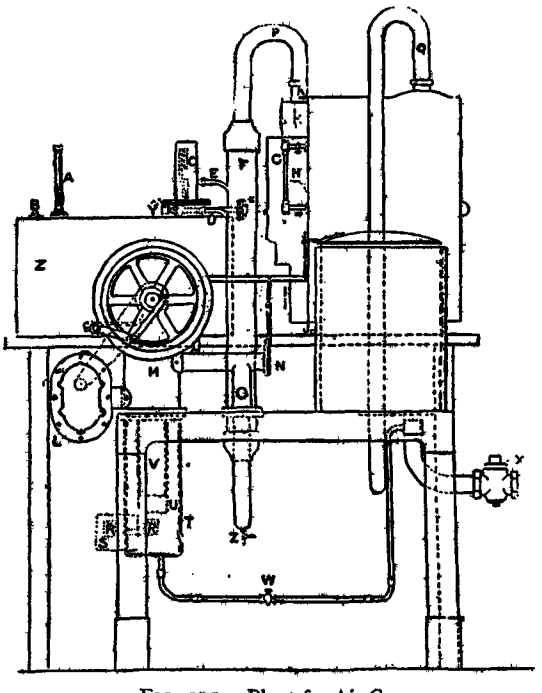


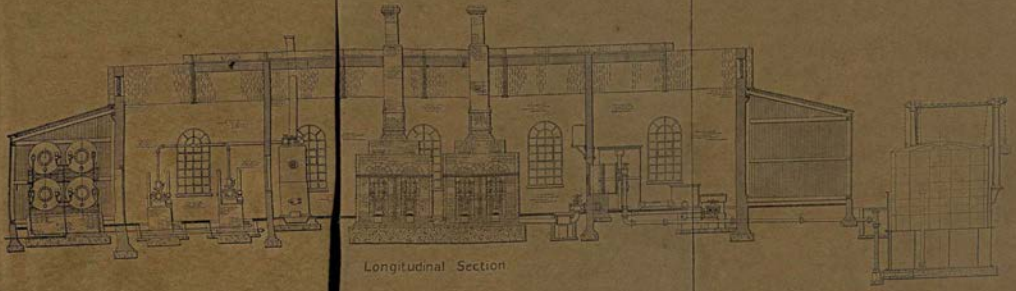
FIG. 175.—Plant for Air Gas.
(The Non-Explosive Air Gas Co. Ltd., London.)

The gas is consumed in burners with small inverted mantles. The oil usually employed is petroleum ether, B.P. 35°-60° C.

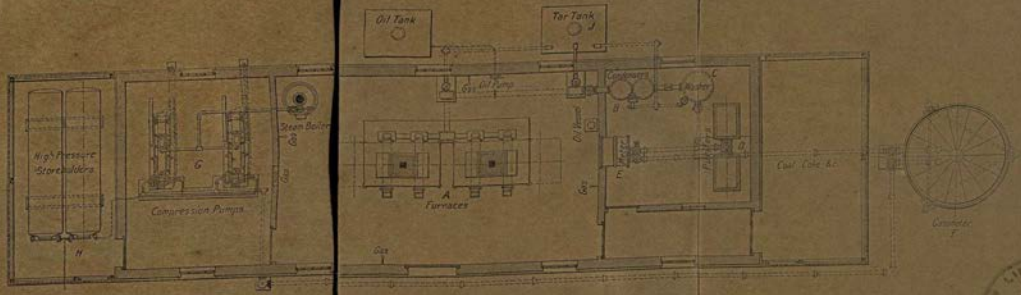
NATURAL GAS

In some parts of the world, especially in America, immense stores of natural gas under great pressure have been obtained, generally when boring for oil. This gas is conveyed in pipes to the various towns where it is required for use, chiefly for metallurgical purposes. The composition is variable.

Pintsch's Patent 10" Oil Gasworks.



Longitudinal Section



Plan.

FIG. 175.

LIBRARY OF THE ROYAL SOCIETY OF ARTS

ACETYLENE

By Frank B. Gatehouse

LITERATURE

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R. Granjon, P. Rosemberg, R. Amédéo and Others.—Brochures and Pamphlets of l'Office Central de l'Acetylene. Paris.

Acetylene, C_2H_2, is the simplest member of the acetylene series of unsaturated hydrocarbons having the general formula C_nH_{2n-2}.

Acetylene is a gas at ordinary temperature and pressure: it occurs in small quantities in coal gas and is produced during the incomplete combustion of methane, ethyl alcohol, coal gas, and other substances.

It may be synthesised from its elements by causing an electric arc to pass between carbon poles in a current of hydrogen.

Acetylene may also be produced by various other methods which have, however, become only of academic interest since the discovery of calcium carbide by Wilson in Canada, and Morissan in France, in 1892. The growth of the carbide and acetylene industry since that date has been phenomenal, and its history forms one of the romances of science.

For commercial and industrial purposes acetylene is now produced entirely by the interaction of calcium carbide (Vol. II.) and water:—

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Pure acetylene is said to be almost odourless, the well-known and distinctive unpleasant odour usually associated with this gas being due to impurities, chiefly phosphorus compounds (see below).

Acetylene has a theoretical specific gravity at 0° C. of 0.9039 (air = 1) which may be compared with Leduc's experimental value of 0.9056. The critical temperature of acetylene is 37° C. and the critical pressure nearly 68 atmospheres. At lower temperatures acetylene is liquefied at a less pressure, but owing to the fact that it is liable to decompose or dissociate into its elements with explosive violence even under a pressure of 2 atmospheres, the manufacture, storage and use of liquefied acetylene is prohibited by law, but this does not apply to "dissolved acetylene," which see.

Acetylene is readily soluble in water, 100 vols. of water dissolving about 95 vols. of C_2H_2 at ordinary temperature and pressure; it is less soluble in brine, lime-water or calcium chloride solution, which facts are occasionally taken advantage of in practice. For details as to solubility in acetone see under "**Dissolved Acetylene,**" p. 405.

Acetylene has an ignition temperature in air of 406°-440° C. (Dixon and Coward). Mixtures of acetylene and air have a very wide range of explosibility ranging from 3.35 to 52.3 per cent. of acetylene by volume. Acetylene is readily polymerised by heating, the chief product being benzene (C_6H_6).

The heat of combustion of acetylene has been determined by various experimenters. It may be stated to be 363 large calories per gramme-molecule. Numerous attempts to determine the temperature of the acetylene flame have also been made. Under ordinary circumstances it may be taken at about 2,500° C. in air, and 4,000° in oxygen (see Welding).

Total heat generated per cubic foot of acetylene is 1,500 B.T.U. (= 14,200 calories per cubic metre = 12,200 calories per kilogram burnt). 2½ vols. oxygen are required, theoretically, for the combustion of 1 vol. acetylene. In welding 1.6 vols. of oxygen to 1 vol. acetylene give best results.

Calcium Carbide is manufactured in the electric furnace, as described in Vol. II., the raw materials being lime and coke or anthracite coal.

The principal impurities to be guarded against in the raw materials are phosphorus, sulphur, silica, magnesia, iron, and alumina, which either give rise to impurities in the evolved acetylene or difficulties in the manufacture of the carbide.

The **storage of carbide** in this country is governed by an Order in Council under the Petroleum Acts, which together with local bye-laws and regulations should be studied by intending users of acetylene.

The Analysis of Calcium Carbide and Acetylene.—In the space at our disposal it is impossible to more than briefly indicate the impurities that should be estimated for technical purposes. Full details as to the methods to be employed will be found in the volumes of *The Acetylene and Welding Journal* mentioned under "Literature" and in Lunge and Keane's "Technical Methods of Analysis."

Apart from the gas-yield of carbide, the question resolves itself into an estimation of the impurities present in the acetylene evolved under proper conditions.

The gas-yield can best be estimated by decomposing a known weight of carbide in a suitable generator, and passing the gas through a standardised meter. All the water employed should be first saturated with acetylene and the mean of several results taken. Owing to the difficulty of sampling, as large a quantity of carbide as possible should be employed; for this reason estimations carried out under ordinary laboratory conditions cannot be relied upon.

The regulations of the British Acetylene and Welding Association which govern the purchase and sale of carbide in this country enjoin that the carbide when broken to standard size (1·2½ in. or larger) shall yield not less than 4.8 cub. ft. per lb. at standard temperature (60° F.) and pressure (30 in.).

A latitude of 5 per cent. shall be allowed for analysis. For other important details the regulations, which may be obtained from the office of the Association, 103 and 104 Cheapside, London, E.C., should be consulted.

The only impurity specified is phosphoretted hydrogen, which must not exceed 0.05 per cent. by volume, with a latitude of 0.01 per cent.

It is desirable also to test for sulphur compounds and ammonia in the acetylene and also to ascertain the temperature and speed of reaction between the carbide and water. The former should not exceed 100° C.

Acetylene for Domestic and Industrial Purposes

Until recent years acetylene was used almost solely as an illuminant for the lighting of private houses, churches, institutions, also less extensively for street and public lighting.

Owing to the great improvements that have been made in the construction of Bunsen burners, it may now be quite satisfactorily employed for heating and cooking purposes, and also in conjunction with specially prepared mantles for incandescent lighting.

The **acetylene motor**, also, is almost if not quite an accomplished fact, but space will not permit of a description here. Acetylene is used largely for **marine signals, beacons, and buoys**, and for temporary lighting with portable generators, "**flare lamps**," etc. Acetylene motors, motor cycles and bicycle lamps are too well known to need any description; it is obvious, however, that owing to contingent circumstances acetylene generated and used under such conditions is placed at a great disadvantage.

Acetylene generators as ordinarily employed for domestic and industrial purposes may be divided into two classes: (1) Non-automatic, and (2) Automatic. These again may be divided into carbide-to-water and water-to-carbide generators.

Briefly, in the non-automatic type a quantity of carbide is decomposed at a stated time, and the whole of the gas liberated is collected in a gas-holder for future consumption; in the automatic type, the carbide is decomposed in limited and stated quantities for immediate consumption, the reaction between the carbide and water being regulated by the consumption of the gas.

A complete generating plant consists of a generator, washer, condensers, gas-holders and purifier, with the necessary connections, valves, etc.

Our illustrations depict (Fig. 176) a non-automatic carbide-to-water plant, also (Fig. 177) the well-known "Carbic" plant in which cakes of carbide are used specially prepared by soaking in oil or fat.

These plants are typical of the classes mentioned and are made by some of the best known acetylene engineering firms in the United Kingdom. The diagrams are self-explanatory. We are indebted to "The Rosco" Acetylene Co., of 130 York Street, Belfast, and "Carbic" Ltd., London, for permission to use these illustrations.

The purifying materials employed, chiefly for removal of the phosphorus compounds, are based either on bleaching powder or chromic acid. The former substance, however, has several drawbacks in use, and is being replaced by the more satisfactory chromic acid compounds.

One of the best known purifiers is "**heratol**" which is stated to consist of an acid solution of chromic acid absorbed in "Kieselguhr." A more recently introduced material is known as "**Catalysol**" (French Patent, 434,137, 12th September 1911, and French Patent, 440,207, 15th February 1912, P. J. Granjon).

This consists of kieselguhr, 350 parts, soaked with a solution of ferrous chloride (40° Bé.), 640 parts; mercuric chloride, 8 parts; precipitated manganous acid, 2 parts. The mixture is exposed to the air until the ferrous salt is completely oxidised, when it forms a yellow powder which may be used until it becomes white. The oxidation and revivification is facilitated, it is claimed, by the incorporation of a small quantity of copper sulphate (or other copper salts) with the liquid or mass.

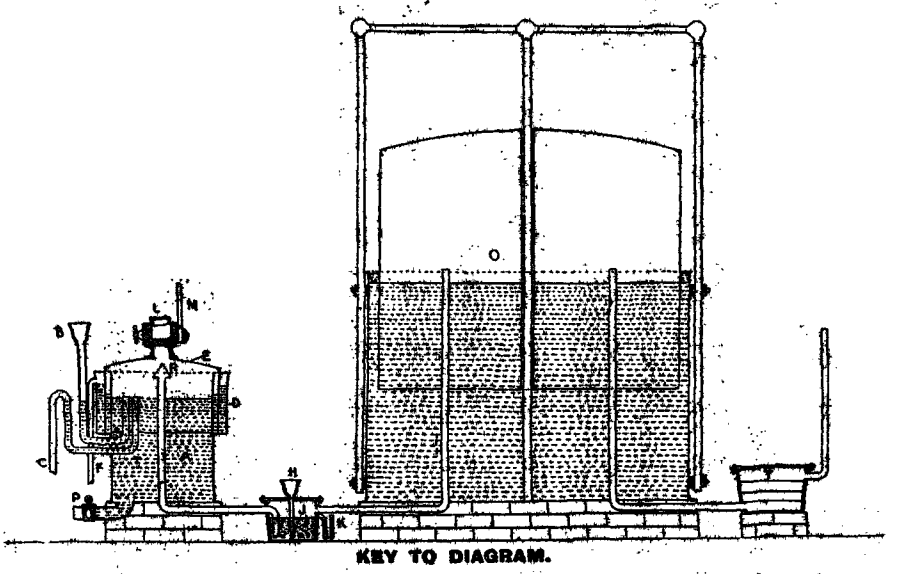


FIG. 176.—"Rosco" Patent Non-Automatic Acetylene Plant.

Key to Diagram.—(A) Generator. (B) Water Inlet to Generator. (C) Overflow. (D) Water Seal. (F) Water Overflow of Seal. (L) Patent Carbide Feed-Valve, which consists of a Hollow Plug Tap with Handle (M); when the Handle (M) is turned upwards the hollow of the Tap can be filled with Carbide; on giving the Tap a third of a turn the Hollow of the Plug is cut off from the outer air and is opened to the Generating Tank so that the Carbide contained in it is discharged over a Distributor (R) unto the Tray (N) which is in the water in the Generating Tank. (P) Cock for removal of Sludge. (J) Scrubber and Seal Pot through which Gas passes to Holder. (H) Water inlet to Scrubber. (K) Overflow of Scrubber. (O) Gasholder. (T) Dry Purifier.

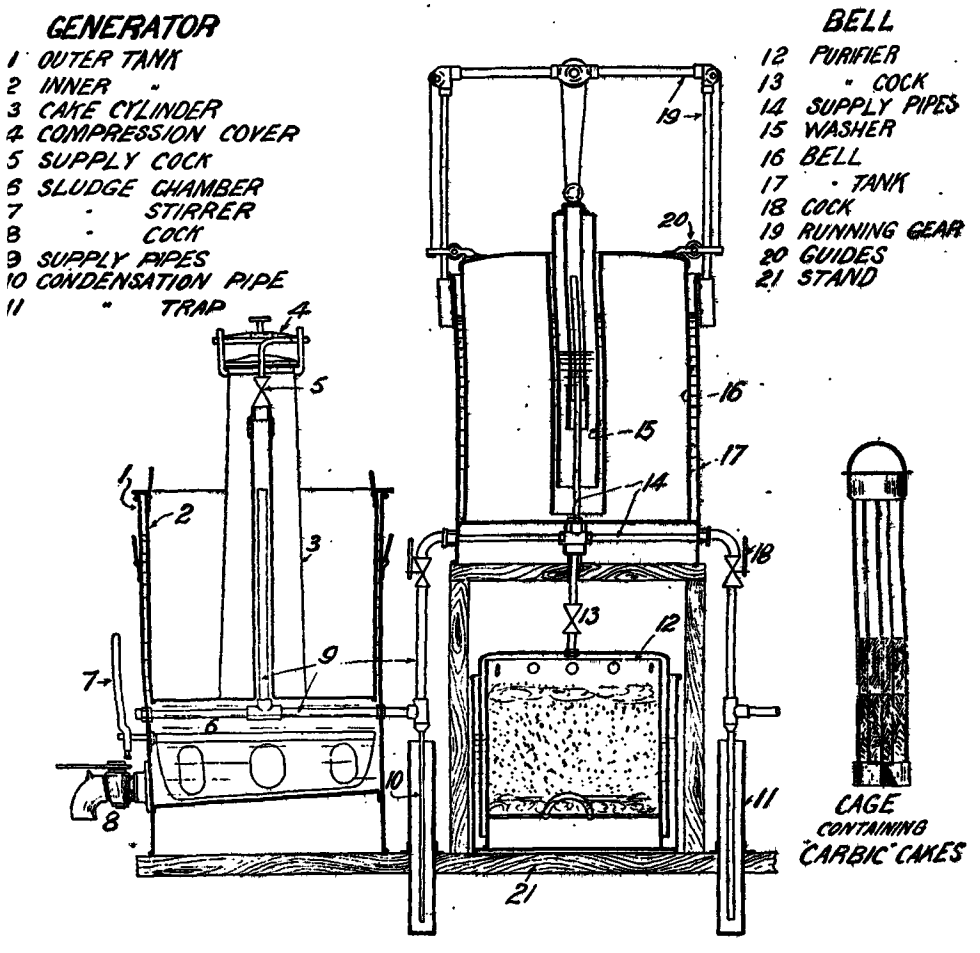
One of the chief advantages of this material is that when exhausted it may be revivified by exposure to air. Both in the case of heratol and catalysol there is a gradual change in colour as the material becomes exhausted, but the degree of purification of acetylene may always be easily ascertained by placing a strip of filter paper soaked in nitrate of silver solution in a stream of the gas as it issues from a burner. If efficiently purified the test paper will not darken.

We have mentioned that acetylene may be used with incandescent mantles with special burners, but the acetylene must be rigorously purified and used at a

higher pressure than when ordinary atmospheric burners are employed. This is not altogether a disadvantage, as the gas may then be more satisfactorily employed for heating and cooking purposes.

The gas is forced into the burner at 80-100 mm. pressure (water column). Burners using 15 and 25 l. per hour give lights = 25 and 40 candle-power respectively.

In this country, however, the use of atmospheric burners such as the well-known "Elta," "Luta," "Cyka," and the "Roni," made by Messrs George Bray & Co., Ltd., of Leeds, are almost exclusively employed. All acetylene generators and apparatus should conform to the regulations of the British Acetylene and Welding Association.



THE "CARBIC" SYSTEM

FIG. 177.

Oxy-Acetylene Welding.—For the autogenous welding of metals and alloys, also for cutting purposes, the oxy-acetylene welding process is making phenomenal progress, and bids fair to eclipse all other welding methods.

For the low-pressure system of welding, the acetylene is obtained from a suitable generator as described above, in the high-pressure system the gas is obtained from a cylinder of dissolved acetylene, under pressure; in both cases the oxygen is generally also obtained from a cylinder. Special welding and cutting blowpipes are employed, also suitable welding rods, and in some cases fluxes are required. The process is of the widest application and is largely used both for con-

structional and repair work, but serious work should not be attempted or permitted without expert tuition and guidance. Welding schools have been formed at many of the chief industrial centres and courses for workmen, works managers and engineers are held regularly.

For further details of the process reference should be made to the works mentioned under "Literature." Welding blowpipes, valves, manometers, etc., may be obtained from the British Oxygen Co., Ltd., Westminster, and most acetylene engineering firms.

FIG. 178.—Acetylene in Acetone. (Acetylene Illuminating Co.)

Dissolved Acetylene.—As mentioned previously acetylene is readily soluble in many organic liquids, notably acetone. Advantage is taken of the fact, and at the same time the difficulties and dangers connected with the manufacture of the compressed gas were overcome, in the manufacture of what has become known as "Dissolved Acetylene." The largest, and until recently the only, firm manufacturing dissolved acetylene in the country is the Acetylene Illuminating Co., of Lambeth Road, S.W. According to their process the washed, cooled, and purified acetylene is pumped under pressure in cylinders apparently filled with a suitable porous material saturated with acetone.

1 vol. acetone takes up, under 12 atmos. pressure, about 100 vols. of acetylene.

Dissolved acetylene is employed chiefly for high-pressure oxy-acetylene welding, motor car and railway carriage lighting, and for marine signals and beacons.

For railway carriage lighting, etc., carburetted acetylene has been employed. This consists of a mixture of acetylene and a hydrocarbon vapour such as benzol, but its employment has not become very extensive.

Acetylene in the Chemical Industry.—The applications of acetylene for lighting, heating, and especially welding purposes are many and varied, notably in the construction of chemical plant and vessels, drums, etc., but apart from these applications acetylene is finding an ever widening field of usefulness as a chemical agent as the basis of new and interesting compounds.

Calcium Carbide, the "raw material" for the production of acetylene, has itself become an important substance in the chemical industry as the starting-point in the manufacture of various compounds of nitrogen such as the cyanamides, cyanides, ammonia, etc. (see Vol. II.).

FIG. 179. The "Roni" Single Orifice Burner.

FIG. 180. "Elta" Burner for Acetylene. Can be turned low like coal gas burners without carbonising.

Acetylene Burners. (Bray.)

The compounds of acetylene with chlorine are already well known. They take the form of more or less volatile liquids, and may replace the highly inflammable carbon disulphide, ether, benzene, etc., in the extraction of fats and oils, etc.

Acetylene tetrachloride or tetrachlorethane may be obtained by the direct union of acetylene and chlorine under the influence of light, but the reaction sometimes proceeds with explosive violence. It is manufactured according to one process by passing acetylene and chlorine alternately through a mixture of finely divided iron and chloride of sulphur. The tetrachloride is distilled off and the residual sulphur converted into the chloride for use again.

Among other processes enjoining the use of acetylene that have been suggested or patented may be mentioned the manufacture of phenol by a process devised by Berthelon, as well as the production of various sulphuric derivatives of acetylene, which apparently, however, have not been carried out on a commercial scale.

By heating a mixture of acetylene with either of the oxides of carbon, or by passing the oxide over heated carbide, free carbon is obtained in the graphitic state. These reactions are stated to be utilised in Frank's process for preparing a carbon pigment. Another process for the production of

acetylene black consists in passing an electric spark through acetylene under pressure. This causes the gas to dissociate with the formation of carbon and free hydrogen. H has been manufactured this way.

In a German Patent (1907) special claim is made for the action of mixtures of acetylene and air in oxygen on a mixture of copper and nickel, as well as on other metals or their oxides or salts,

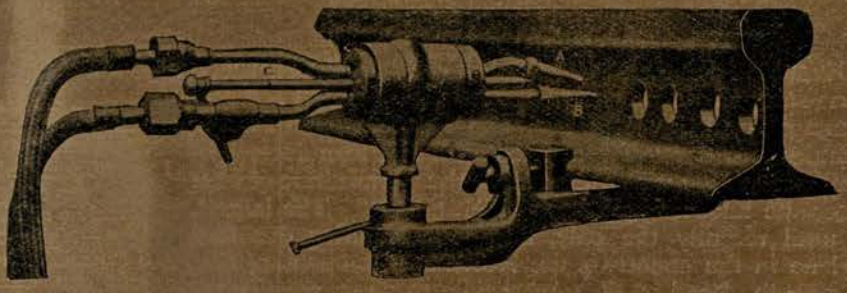


FIG. 181.—Oxy-Acetylene Flame used as Rail-Piercer. A is Oxy-Acetylene Heating Jet, B is the Oxygen Jet, C is the Centering Bit; A and B Revolve. (Carbic Ltd., London.)

whereby plastic masses are obtained. The products contain only very small proportions of the metal (less than 0.2 per cent.) which manifestly acts as a catalyst.

It has been proposed to manufacture alcohol on the commercial scale by making use of the reaction that takes place between hydrogen and acetylene in the presence of platinum black, but the cost would be prohibitive. The following processes, however, have a direct bearing on this problem.

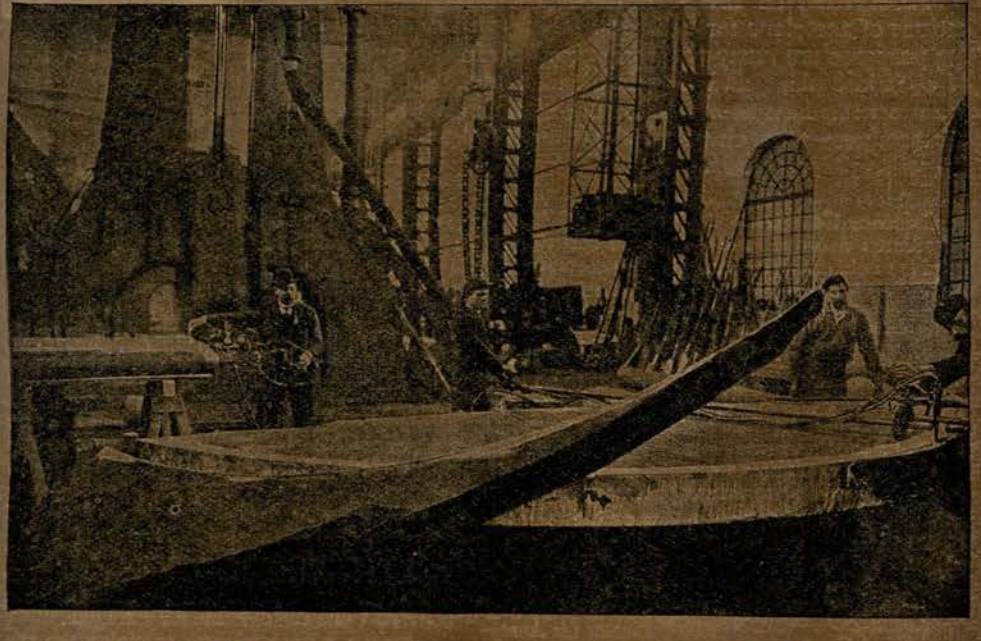


FIG. 182.—Cutting Armour Plate 9 inches thick with Oxy-Acetylene Flame. (Supplied by Carbic Ltd., London.)

According to a French Patent (1910) acetylene and hydrogen are separately generated, and then mixed and heated under a suitable pressure, ethylene being formed, which is then converted into ethyl hydrogen sulphate by the action of sulphuric acid in a special apparatus.

In the second process, for making acetaldehyde and its condensation products and polymers, a current of acetylene is passed into a solution of a mercuric salt in at least 45 per cent. sulphuric acid.

or in at least 25 per cent. phosphoric acid, preferably at ordinary temperatures (below 70° C.), but the temperature required varies with the strength of the acid solution.

The formation of higher condensation products, such as crotonic aldehyde, is greater the higher the concentraton of acid used. The process can be stopped at intervals in order to separate the products by distillation, or the aldehyde may be precipitated by the addition of a neutral salt. It is advisable to carry out the reaction preferably in an atmosphere of acetylene, and to keep the liquid well cooled during the process.

In conclusion it may be mentioned that calcium carbide, acetylene, and its derivatives, are being studied by the chemists of all nations, and although in the majority of cases the results so far obtained have not been of great commercial value, these researches may have an important bearing on the future of the acetylene industry.

INCANDESCENT GAS LIGHTING

By Ernest A. Dancaster, B.Sc.

The manufacture of incandescent gas mantles is described in Vol. II. It suffices to say that a mantle consists of a skeleton of silica impregnated with a mixture of 99 per cent. thoria and 1 per cent. ceria.

Until 1891 Welsbach's mantles were scarcely successful, but in that year he succeeded in obtaining the cerium and thorium rare earths in a perfectly pure condition, and made the remarkable discovery that while pure ceria and pure thoria scarcely yielded more light than other incandescent solid bodies, yet a mixture of the two in the above proportions yielded an intensely brilliant light. The cause of this phenomenon is not understood; it is certainly not a pure temperature effect; the presence of the trace of ceria seems in some catalytic manner to enable the thoria to convert more heat energy into light energy than properly corresponds to its actual temperature ("luminescence"). Moreover, this effect is only displayed in burning gases.

In the old "*vertical*" Welsbach burner the mantle is suspended in the hottest part of a Bunsen flame by means of an asbestos thread slipped over the top of a vertical rod. With a gas consumption of 3¾-4½ cub. ft. per hour it gives a light initially of 80-100 candle-power, but sinking to 60 candles after some time. The mantle has an average life of 1,000 burning hours.

During recent years inverted burners and mantles have come very largely into use. The mantles are considerably smaller and last longer, while the light efficiency is greater than in the case of the upright mantle.

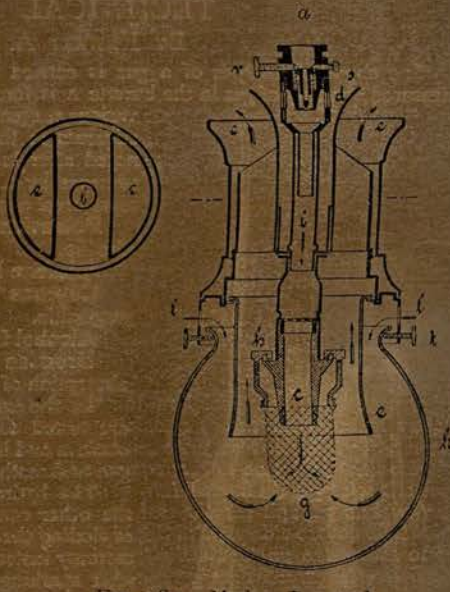


FIG. 183.—Modern Inverted Incandescent Burner.

Fig. 183 shows a modern inverted burner. The gas enters at *a*, the supply being regulated by the screw *r* and the proper amount of air is mixed with it by the hole at *d*. Passing through the tube *b* the gas reaches the fireclay tube *c* on which the mantle *g* is supported at *h*. Here it burns, a supply of fresh air being sucked in from outside through *ll*. The hot burnt gases now stream up past the tubes carrying the incoming supply of gas (thereby preheating the entering gas and effecting a great economy in heat much after the manner of the regenerative furnace), finally escaping into the air at *cc*. *k* is a glass globe. Such a light yields 80-100 candle-power for a gas consumption of only 3-3.2 cub. ft. per hour.

The above discussed burners are suitable for ordinary gas supplies delivered under a pressure of 1 in. water column (25 mm. say).

Where intense lighting is required, as in the case of street lamps of 1,000-5,000 candle-power, this is obtained by using various patterns of high pressure and intensifying burners in conjunction with apparatus for increasing and regulating the pressure of the gas supply.

In Berlin the gas is supplied at several stations at a pressure of 1-1½ metres (3¼-5 ft.) water column. It should be noticed that with the advent of the incandescent mantle quite non-luminous flames, *e.g.*, that of water gas, methylated spirit, etc., can be used. The problem of using petroleum lamp oil for generating hot non-luminous flame for use with the incandescent mantle has not yet been entirely solved, but it can be shown that were this done it would furnish one of the cheapest sources of light.

The introduction of recent improvements in electric lighting, especially the introduction of metal filament lamps (tantalum, osmium, wolfram), has put new life into the industry, and has again made electric lighting capable to compete with gas for private houses.

The Hewitt or Hermes quicksilver lamp gives a greenish flame very rich in ultra-violet rays,

and consequently much used for medical purposes, testing the fastness of dyes to light, for photography, etc.

For intensive lighting the electric arc is still the cheapest, as the following table shows:—

Source of Light.	Candle-Power.	Cost per Hour.*	Cost per Candle-Power per Hour.*	Gas or Power Used per C.P. Hour.	Heat Evolved per C.P. Hour.
Coal gas—		*d.*	*d.*		Cals.
Wenham lamp	110	0.64	0.0058	3.7 l. gas	20
Incandescent mantle, vertical	80	0.18	0.0023	1.5 ,,	8
,, ,, inverted	80	0.14	0.0017	1.1 ,,	6
Alcohol incandescent light	60	0.44	0.0073	2 g. alcohol	13
Acetylene gas	25	0.28	0.0112	0.6 l. C_2H_2	8
Petroleum oil lamp	25	0.18	0.0072	3 g. petroleum	30
Electric light—					
Carbon filament lamp	25	0.30	0.012	3.2 watts.	1-3
Osram lamp	50	0.20	0.004	1.1 ,,	1-3
Glass globe arc light	400	1.4	0.0035	0.8 ,,	<1
Naked arc light	1,500	1.8	0.0012	0.3 ,,	<1

* Varies with locality.

TECHNICAL GAS ANALYSIS

By Ernest A. Dancaster, B.Sc.

The chemical analysis of a gas is carried out by **Hempel's gas apparatus** (Fig. 184). A measured quantity of gas in the burette A is forced by means of a pressure-tube C into contact with various reagents contained in the pipette B, whereby various constituents in the gas are absorbed, and the diminution in volume noted after bringing the gas back to A and restoring the original pressure by C. A separate pipette is used for each reagent, the most usual absorbents being:—

Potassium Hydrate Solution for the absorption of carbon dioxide.

Alkaline Pyrogallate Solution for the absorption of oxygen.

Cuprous Chloride Solution for the absorption of carbon monoxide.

Alcohol for the absorption of hydrocarbons.

Bromine Water (or **Fuming Sulphuric Acid**) for the absorption of olefines.

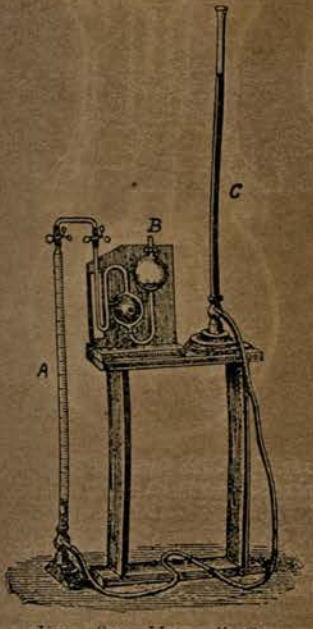


Fig. 184.—Hempel's Gas Apparatus.

In the examination of coal gas, oil gas, etc., the constituents are tested for in the following order: (1) Carbon dioxide; (2) olefines and benzol; (3) oxygen; (4) carbon monoxide; (5) hydrogen and methane; (6) nitrogen.

The hydrogen and methane are burnt (after the removal of the other constituents) by mixing with an excess of oxygen and exploding the mixture in a Hempel explosion pipette containing mercury instead of an aqueous solution. The decrease in volume after sparking gives the quantity of hydrogen, and the further decrease in volume due to the absorption of carbon dioxide by potassium hydrate solution gives the quantity of methane originally present, since the combustion of a given volume of methane gives the same volume of carbon dioxide, according to the equation—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

The volume of nitrogen is then found by difference.

For water-soluble gas, *e.g.*, NH_3, H_2S, mercury is used in the pressure tube burette. Ammonia in small quantities is determined by $\frac{N}{10}$ H_2SO_4, and sulphur obtained by burning with O to H_2SO_4, in special apparatus. More than 0.1 g. NH_3 and 0.5 g. S per cubic metre is inadmissible. The specific gravity of the gas is determined in special gas balances.

The most poisonous constituent of coal gas is the carbon monoxide, which when breathed to the extent of 0.1-0.2 volume per cent. (=2 volumes per cent. coal gas) causes headache, insensibility, and ultimately death.

PHOTOMETRY

By Ernest A. Dancaster, B.Sc.

The measurement of the illuminating power of two sources of light is important (photometry), and is determined by means of photometers.

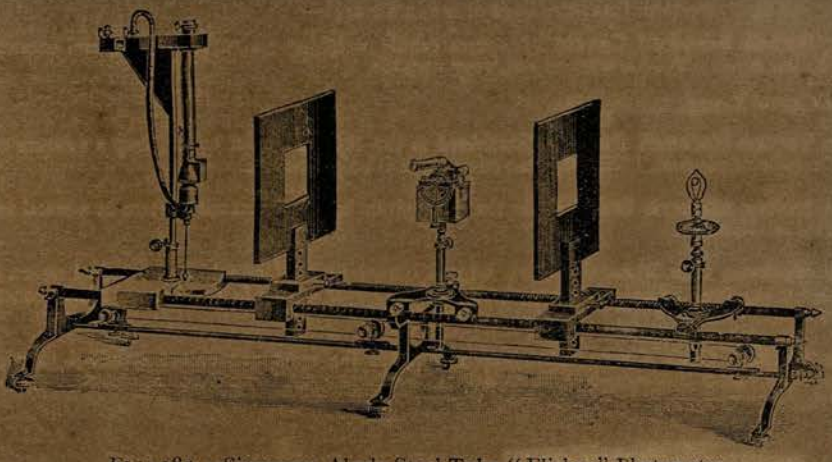


FIG. 185.—Simmance-Abady Steel Tube "Flicker" Photometer.
(A. Wright & Co., London.)

The most common forms of modern photometers are varieties of the old "Bunsen" or "grease spot" photometer, which consists of a white, unglazed paper screen with a grease spot at the centre. The two sources of light are placed on opposite sides of the screen, and the latter is then moved about between the two lights until the grease spot appears equally illuminated with the rest of the screen, from whichever side it is viewed. The illuminating powers, L_1 and L_2, are then given by the equation :—

$$\frac{L_1}{L_2} = \frac{d_2^2}{d_1^2},$$

d_1 and d_2 being the respective distances of the lights from the screen.

"Flicker" photometers are especially useful for comparing lights of different colour. In the Simmance-Abady "flicker" photometer a white sighting wheel (Fig. 186) with eccentric bevelled edges is caused to revolve, by means of clockwork, between the two lights under examination. Above the wheel is a total reflecting prism and a short horizontal telescope, the whole forming the photometer head. On looking through the telescope the upper portion of the edge of the sighting wheel is seen as a *disc*. As long as the illuminations of the two sides of the edge of the sighting wheel are unequal the disc will be seen to flicker, but when the wheel is brought into such a position (by sliding the photometer head along a bar between the lights) that the illuminations are equal, the flickering ceases, and a steady disc is obtained. The reading is then taken. The bar is graduated in candles power so that if a standard of unit power is employed, no calculation is necessary. Fig. 185 shows the instrument.

FIG. 186.—Sighting Wheels for Simmance-Abady "Flicker" Photometer. (A. Wright & Co., London.)

The Lummer-Brodhun photometer is another modern type of photometer, the characteristic feature of which is an optical device for viewing both sides of the screen at once, the light reflected from them being seen as two adjacent fields of vision.

Light Standards.—It is necessary to choose some source of light as a standard, and to express the illuminating values of all other sources of light in terms of this standard. The original standard chosen was a candle burning at a given rate, hence the illuminating power of all sources of light is always expressed in candle-power.

The chief light standards that have been or are in use are :—

The British Standard Candle is a sperm candle weighing six to the pound, and consuming 120 grains per hour. Troublesome to use, very variable.

The Carcel Lamp, burning colza oil.

The Vernon-Harcourt Pentane Standard is the light obtained by burning a mixture of air and the vapour of pentane. Troublesome to use, but is very constant.

The Hefner-Alteneck Standard is the light given by burning amyl acetate in a metal lamp. Much used in Germany.

The Methven Gas Standard is an Argand burner in front of which is a metal screen with a rectangular aperture. Coal gas is consumed at the rate of 5 cub. ft. per hour. Fairly constant, easy to use.

The Electric Glow Lamp Standard is perhaps the most convenient standard to use for ordinary work, but it is necessary to frequently re-standardise the lamp if the results obtained are to be reliable.

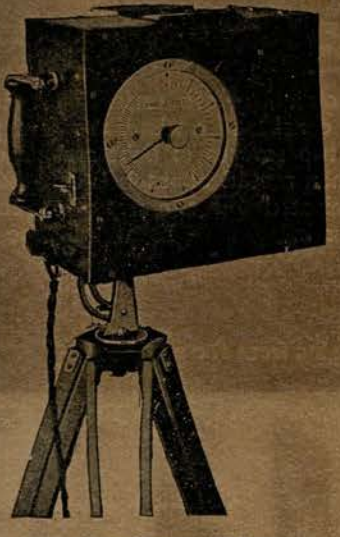


FIG. 187.—Trotter Universal Portable Photometer. (Everett-Edgcumb, London.)

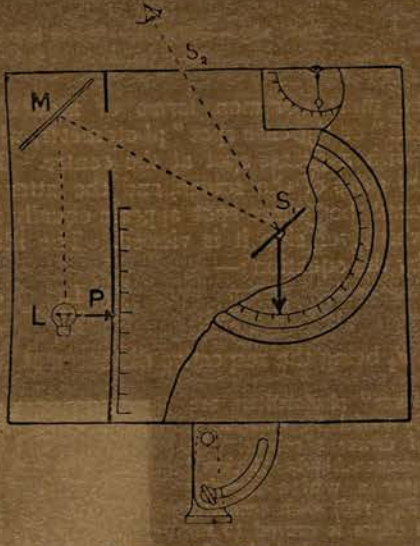


FIG. 188.—Section of Trotter Photometer. (Everett-Edgcumb, London.)

The Violle Platinum Standard is the light given normally by 1 sq. cm. of platinum raised to its point of fusion and about to solidify; extremely constant; used as a primary standard in important work, but unsuitable for ordinary commercial photometry.

When the illumination of a surface—not a source of light—such as the platform of a railway station or a street, is required, the results are expressed in candle feet, the unit of measurement being the illumination of a white surface by a standard candle at a distance of one foot.

A portable photometer is used for this purpose, such as the "Everett-Edgcumb Universal **Trotter" photometer.** It consists of a small box mounted on a tripod in a similar manner to a camera. Within the box is a small electric glow-lamp L. A trigger or spring-key when pressed lights the lamp. The light from the latter is reflected by means of a mirror S_1 on to a white screen M, which may be turned round by means of a milled head so as to reflect varying amounts of light through a narrow hole S_2 in a second white screen let into the face of the photometer. The light falling on the face of the photometer illuminates the outside face of this screen, and the milled head is turned round until a balance is obtained between the illuminations of the two screens, *i.e.*, until the hole in the second screen S_2 appears neither lighter nor darker than the rest of the screen. A pointer is attached to the milled head of the first screen, and this indicates on a scale the illumination in candle feet. Usually the instrument is used with the face horizontal, but it may be also used

to test the candle-power of a source of illumination. In this case the face is turned directly towards the light. The value obtained in candle feet is multiplied by the square of the distance of the source of light from the photometer, and the candle-power of the former is thus obtained.

A recently introduced portable photometer for measuring surface illumination is the "**Holophane Lumeter**" of Messrs R. & J. Beck Ltd., and is noteworthy on account of its small size, its accuracy, and the ease with which it can be used; it consists of a small box $8\frac{1}{2} \times 2\frac{3}{4} \times 2\frac{1}{2}$ in. divided into two chambers. One chamber A is coated with a matt white surface and contains an electric glow-lamp lit by means of a small two-cell accumulator. The other B is a dark chamber and contains a white screen C with a small aperture D. A side tube provided with a focussing eyepiece enters the chamber B obliquely, by means of which the screen can be seen and also—through the central aperture of the screen—any illuminated surface in front of the photometer.

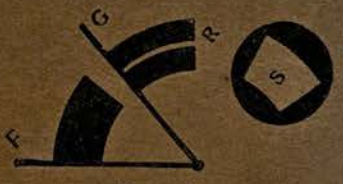


FIG. 189.

The partition between the two chambers has a sector-shaped opal glass window E, through which the light from the glow-lamp illuminates the annular white surface of the screen C. The amount of light falling on this surface can be varied by means of two opaque sectors which can be moved across the face of the window by two levers F, G, which also act as indicators, placed at the end of the photometer. One of the sectors is capable of closing the whole aperture with the exception of a segmental band across the centre, thus reducing the illuminated area from 1 to $\frac{1}{10}$; the other sector closes this segmental band, thus reducing the area from $\frac{1}{10}$ to $\frac{1}{100}$. Thus one of the indicators reads in $\frac{1}{10}$ths and the other in $\frac{1}{10}$ths of a candle foot, the whole range of the scale being from $\frac{1}{100}$ to 1 candle foot. For measuring illuminations greater than 1 candle foot slides containing dark glasses are introduced. These are slid into position by means of the knobs H, H. On introducing one of the slides the scale reading is multiplied by 10, and on introducing the second slide the reading is multiplied by 100. Thus in the first case readings from $\frac{1}{10}$-10 candle feet are obtained, and in the second case readings from 1-100 candle feet. The total range of the instrument is, therefore, from $\frac{1}{100}$-100 candle feet.

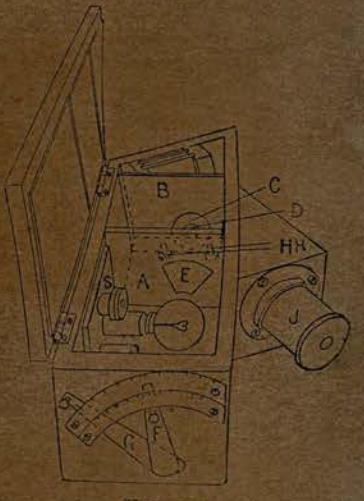


FIG. 190.

"Holophane" Lumeter. (R. & J. Beck Ltd., London.)

A white screen and a standard candle are supplied with the outfit by means of which the instrument can be readjusted when necessary.

In order to use this instrument it is held in the hand and pointed to the object the illumination of which is to be tested. The observer then looks through the eyepiece and sees the illuminated surface through the circular aperture in the screen C. The intensity of the illumination of the annular white surface of the screen is then regulated by means of the indicators F, G until it equals that of the object viewed through the central aperture. The value of the illumination is then read off on the scale. If the illumination is too great recourse is had to one or both of the slides described above.

A good portable photometer is the **Dibdin**.

It should be particularly noted, however, that since the introduction of incandescent lighting it is not so much the illuminating power of a naked gas flame as its heating value which is important. This should be never less than 5,000 calories per cubic metre, and is determined by burning it in special calorimeters.

SECTION XII

Industry of Coal-Tar and Coal-Tar Products

INDUSTRY OF COAL-TAR AND COAL-TAR PRODUCTS

LITERATURE

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DAMMER.—"Handbuch der Chemischen Technologie." Bd. iv. 1898.
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See also under **Synthetic Dyes.**

COAL-TAR

COAL-TAR is the thick, black, evil-smelling liquid (sp. gr. 1.1 to 1.2) which accumulates in the hydraulic mains, condensers, and scrubbers of gasworks. Much, however, is now obtained from the coke ovens used for making hard coke for metallurgical purposes, and this source may eventually become the predominant one here, and has already become so in Germany, who derives two-thirds of her supply from this source.

In 1907 England produced 858,000 tons of tar; Germany, 850,000 tons (1909); France, 170,000 tons (1904); United States, 200,000 tons (1904).

In 1913 England exported the following quantities of coal-tar and coal-tar products:—

		Value.
Crude coal-tar	88,000 cwt.	£16,000
Refined coal-tar and varnish	3,071,000 gals.	68,600
Pitch	9,731,000 cwt.	1,100,000
Tar oil, creosote	36,758,000 gals.	592,000
Coal-tar naphtha	515,000 ,,	24,600
Naphthalene	86,000 cwt.	37,700
Anthracene	564,000 lbs.	1,400
Benzol and toluol	6,655,000 gals.	303,000
Carbolic acid (phenol)	168,900 cwt.	190,000
Aniline and coal-tar oils	1,351,000 lbs.	28,900
Total value		£2,362,200

The United States in 1910 imported 37,000 barrels (280 lbs. per barrel) of tar and pitch, of value $92,000. The export was: 1906, 24,700 barrels; 1908, 96,400 barrels; 1910, 110,500 barrels (280 lbs. to the barrel). Value in 1910 was $138,800.

Coal-tar is the primary raw material of the colour industry. It has an extraordinary complex constitution, which varies not only with the nature of the coal or coke distilled, but also with the temperature of distillation.

The constituents employed in the colour industry are benzene, toluene, xylene, naphthalene, anthracene, phenol, and cresol. The composition is approximately given by the following table:—

	Gas Tar.	Tar from Coke Ovens.		Gas Tar.	Tar from Coke Ovens.
	Per Cent.	Per Cent.		Per Cent.	Per Cent.
Light benzol - -	1.5-2	0.1-0.5	Pyridine bases - -	0.25	0.25
Heavy benzol - -	0.5-1	0.5-1	Heavy oils - - -	20	20
Phenol - - -	0.5-1	0.5-1	Pitch - - - -	50-60	50
Naphthalene - -	4-6	6-9	Finely divided carbon	20	10
Anthracene - -	0.5	0.25			

Coal-tar Distillation

In order to isolate valuable products, the tar is distilled. The still A is of iron and usually holds 20 tons of tar. It consists of an upright cylinder, of nearly equal height and diameter, with a dome-shaped top and a concave bottom, the whole firmly set in brickwork and heated by a fire grate. If coke is employed as heating fuel, the bottom of the still must be completely protected by a curtain arch. The tar must, previous to distillation, have been completely separated from water by long standing, otherwise frothing during distillation ensues.

The distillate passes through a condensing coil BB, placed in a tank C, and is cooled as the distillation proceeds first with cold and afterwards with hot water, in order to prevent the tube blocking up with crystalline solid matter; the condensed liquids pour through the swan-neck pipe *d* into the glass jar *f*, while the permanent gases escape through *ee*. The glass jar *f* allows the rate at which the liquids distil to be observed, and the density of the distilling liquid may be read off by means of a hydrometer placed within it; also samples may be withdrawn from it as required. When the liquids become too hot it is replaced by an iron funnel. From *f* the liquids run into a receiver *g*—an air-tight iron tank, provided with as many cocks f_1, f_2, f_3, f_4, etc., as there are fractions to collect. The different fractions are collected in *g* and are run off successively down different cocks into different iron store tanks.

After the temperature reaches 270° (when the anthracene oils begin to come over) the still is evacuated by a steam pump, which aspirates both gases and oils

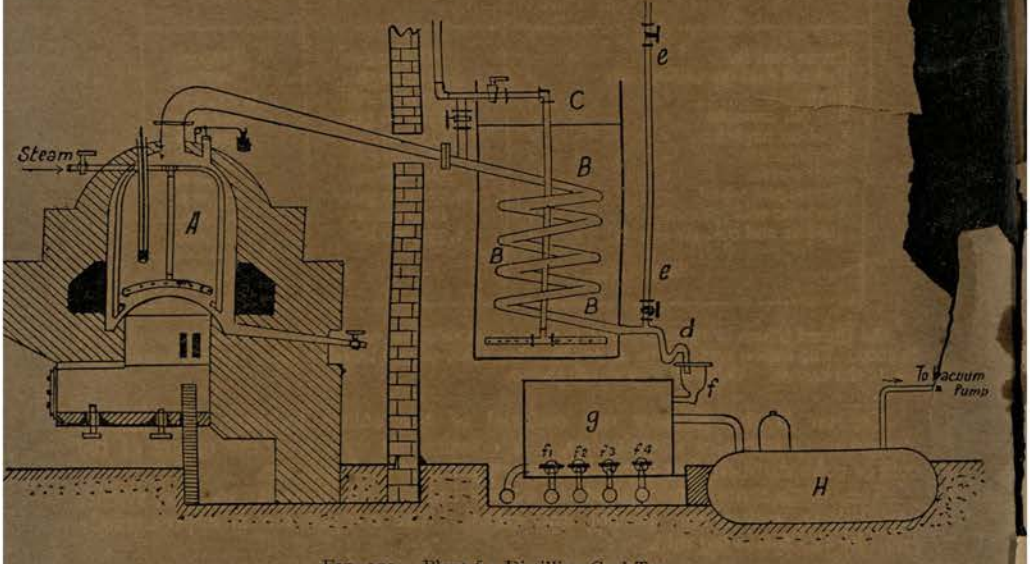


FIG. 191.—Plant for Distilling Coal-Tar.

away from the condensing worm into a large boiler H, sunk in the ground, which retains the anthracene oils, while the gases are forced out by the pump. Simultaneously a stream of steam is blown through the still in order to avoid the setting fast and coking of the layers of pitch in immediate contact with the bottom. If much free carbon is present the still is evacuated after a temperature of 150° C. is reached.

Stills are also now in use whereby a *continuous* process of distillation takes place, the crude tar oil being run in continuously at one end, and pitch run out of the other, while intermediately the various oils are distilled off. For details see the Patent literature, an account of which is given in Lunge's "Coal-Tar and Ammonia."

By means of this distillation the tar is separated into the following portions :—

	Temperature of Distillation.	Per Cent. of Tar.	Specific Gravity.
1. Light oil	Up to 170° C.	2-8	0.90-0.95
2. Middle or carbolic oils	170°-230° C.	8-10	1.01
3. Heavy or creosote oils	230°-270° C.	8-10	1.04
4. Anthracene oils	270°-400° C.	16-20	1.10

In the still there remains behind a residue of pitch (50 per cent.).

1. **The Light Oils**, sp. gr. 0.9-0.95, are redistilled, and the fractions boiling over 170° C. added to the middle oils. Then the liquid is agitated in the cold with 5 per cent. of concentrated H_2SO_4 in cast-iron or lead-lined wooden vessels, whereby bases are fixed, while unsaturated hydrocarbons, phenols, and sulphur compounds are dissolved or resinified. The dark acid layer is drawn off and worked up for ammonium sulphate. The oil is then washed with water and dilute caustic soda, dried, and fractionally distilled, and the fractions collected in four portions, viz., (1) the first runnings; (2) between 70°-140° C. (light benzol); (3) 140°-170° (heavy benzol); (4) over 170° C.

The first runnings consist principally of carbon disulphide, pentane, hexane, and aceto-nitrile.

The "crude benzol" thus obtained is rectified in a special still and separated into pure **Benzol**, C_6H_6, B.P. 80° C.; toluene, $C_6H_5CH_3$, B.P. 110° C.; and xylene, $C_6H_4(CH_3)_2$, B.P. 138°-142° C. The hydrocarbons distilling after the xylene (viz. cumene) go to form "solvent naphtha."

The stills used in fractionating are similar to those used in distilling spirits. One of the most efficient is the **Savalle** column as improved by Heckmann of Berlin (German Patent, 39,557). For further details see Martin's "Industrial Chemistry," Vol. I. p. 295 *et seq.*

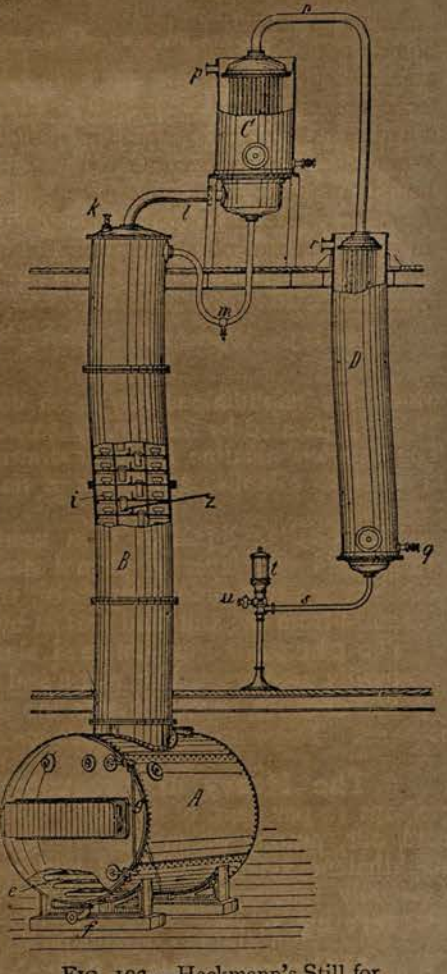


FIG. 192.—Heckmann's Still for Fractionating Light Oils.

The crude benzol is placed in the wrought-iron boiler A (Fig. 192, Heckmann's still) and heated to boiling by means of steam coils; the vapours pass up the iron column B, which is divided into a series of compartments. The vapours pass into each compartment through the raised mouthpiece *i*, passing through the layer of liquid condensed in the compartment and maintaining it in continuous ebullition, while the excess of liquid overflows through a drop-pipe Z and discharges into the compartment below. Finally, the vapours reach the condenser C, where they are still further (but not completely) condensed to a liquid form by means of a water jacket; the condensed liquids, pouring back through the U-tube, pass into the column B, maintain every compartment in B with its proper layer of boiling liquid. The more volatile parts pass on through *n* into the condenser D, where they are completely condensed by means of a water cooling jacket, and the separate fractions run off in succession through *s t n*.

The pure benzol and toluol thus obtained are used for making coal-tar dyestuffs. The 90 per cent. benzol is used (mixed with petroleum ether) for motor cars, for carburetting illuminating gas, and as a cleansing solvent in laundry works. Solvent naphtha finds an extensive application in dissolving caoutchouc in the manufacture of waterproof stuffs.

2. **The Middle Oils,** B.P. 170°-230° C.; sp. gr. 1.01.—These contain much naphthalene and phenols.

The **naphthalene** is obtained by allowing the oil to stand, when large quantities crystallise out and are separated by centrifuging and pressing.

To obtain the naphthalene pure it is melted with 5 per cent. concentrated H_2SO_4, the acid drawn off, and the naphthalene distilled. Sometimes instead of being distilled the naphthalene is sublimed by placing in a shallow iron pan *a*, heated by the steam coil *b*, when the vapours sublime into the large chamber *c*.

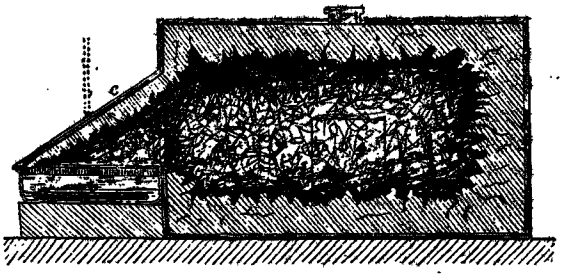


FIG. 193.—Apparatus for Subliming Naphthalene.

For recrystallising naphthalene the ordinary solvent is petroleum spirit, and the operation is carried out in enamelled iron vessels provided with reflux condensers and heated by steam. The crystals are centrifuged and dried in air.

The naphthalene thus obtained is practically chemically pure, occurring in large crystalline plates, M.P. 79° C.

The mother liquors from which the naphthalene has been separated contain 30-40 per cent. of phenol. This is separated by fractionally extracting with a 10 per cent. caustic soda solution. The aqueous alkaline liquid is drawn off from the oil, and steam blown through in order to volatilise any traces of naphthalene or other hydrocarbons that it still contains.

The alkaline liquid is then neutralised by sulphuric or carbonic acid, the precipitated oily layer of phenol drawn off and fractionally distilled from stills with zinc or silver condensing coils; the distillate is crystallised out in the cold, and separated from the still fluid cresols by a centrifugal machine.

The **phenol** is thus obtained almost chemically pure as a white solid. It is principally used for making picric and salicylic acid (pp. 423, 430).

The **cresols,** separated from the phenol, occur as a fluid mixture of the three isomers. These bodies are much used for disinfecting purposes.

3. **The Heavy or Creosote Oils,** B.P. 230°-270° C., sp. gr. 1.04, form perhaps 10 per cent. of the tar. They consist of a complex mixture of neutral and acid oils, among which may be mentioned naphthalene, dinaphthylene, methylnaphthalene, xylenol, naphthol, and paraffins. They are used for creosoting timber—especially telegraph poles and the sleepers of railways. See under **Timber Preserving,** p. 190.

4. **Anthracene Oils,** B.P. 270°-400° C., sp. gr. 1.10, forming 12-17 per cent. of the tar, contain a certain amount of carbolic acid and a considerable amount

of **anthracene**, $C_{14}H_{10}$, M.P. 213° C. This latter is one of the most valuable constituents of coal-tar. To isolate the anthracene and free it from impurities the oil is cooled and the greenish crystals of impure anthracene which separate out are freed from the oily mother liquor by pressing or placing in a centrifugal machine. It then contains only 10-12 per cent. pure anthracene, being mixed with impurities such as phenanthrene, methylanthracene, diphenyl, naphthalene, pyrene, retene, carbazol, etc., which are exceedingly difficult to get rid of. To do this the whole is pressed to 200-300 atmospheres in a hydraulic press heated by steam. Most of the phenanthrene and naphthalene flows away in a liquid form, and the percentage of anthracene is increased to 28-40 per cent.

The anthracene is then washed with *solvent* naphtha. By washing with the pyridine *bases* mixed with solvent naphtha the carbazol is almost completely removed, and a product consisting of 90 per cent. anthracene is obtained, and made into alizarin.

Chemically pure anthracene is obtained by grinding up with caustic potash and lime, distilling, washing with solvents, and subliming.

The plant usually used for subliming anthracene is shown in Fig. 194. The anthracene is placed to the depth of 2-3 in. in a shallow iron pan C, heated from below. Superheated steam from the pipe B, which is perforated by many holes, carries away the vapours into the large chamber D, where they are suddenly chilled by a spray of cold water from the rose H, causing the anthracene to precipitate in the finest state of division—a necessary condition for its easy conversion into anthraquinone by the action of oxidising agents.

5. **Pitch.** — The residue which remains in the tar still is **Pitch** and forms 50-55 per cent. of the tar. Much of it probably consists of finely divided coal or coke, but undoubtedly 20-30 per cent. consists of solid unsaturated hydrocarbons, which give it its distinctive properties. Soft pitch has C = 91.8 per cent., H = 4.6 per cent.; hard pitch has C = 93.2 per cent., H = 4.4 per cent. "**Hard Pitch**" is obtained by carrying the distillation as far as possible. It softens over 100°. **Soft Pitch** is obtained by a shorter distillation. The pitch is always run off while fluid from the still.

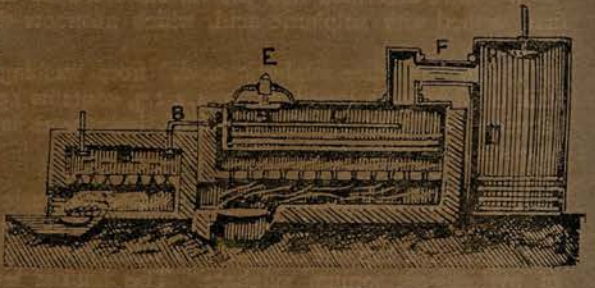


FIG. 194.—Anthracene Subliming Plant.

It is used for making briquettes from coal dust, for making varnishes and blacks (by mixing with certain oils), for making dolomites, stones, etc., in iron-works, and to a certain extent for paving streets, etc.—the natural asphalt being, however, both cheaper and better for the latter purpose.

Testing of Coal-tar and Pitch

(See Watson Smith, *Journ. Soc. Chem. Ind.*, 1883, p. 496.)

1. Free tar from water by placing a large glass beaker immersed in hot water and covered with a glass plate. After one and a half days decant off watery layer on surface.

2. Determine specific gravity by weighing accurately at 15° C. a given volume (say 1 l.) run into a standard flask.

3. Distil 2½ l. of tar freed from water as above from a large glass retort in usual way, placing apparatus on a large iron tray covered with ½ in. of sand (to diminish danger from fire), forcing in a slow current of air through a drawn out tube through the cork and reaching to the centre of the flask.

(*a*) First heat slowly to 60°-70° C., heating at that temperature for a day or two to expel ammonia water.

(*b*) Collect (1) Light oil, up to 170°; (2) Middle oil, up to 230° C.; (3) Creosote oil, up to 270° C.; (4) Anthracene oil.

The volumes of the different distillates are measured, and after treating the fractions much as they are treated on the large scale in the distillation of coal-tar, an estimate of the various proportions of the different substances likely to be obtained in the large scale distillation is arrived at and so the value of the coal-tar judged.

The **Free Carbon** in coal-tar is estimated (Kraemer) by extracting the coal-tar with forty times its weight of xylene, drying the residue at 100° C. and washing. The more free carbon, the thicker the tar and the greater the danger of frothing over during the distillation.

The **estimation of water** in tar is carried out by distilling 500 c.c. of carefully sampled and thoroughly agitated tar from a copper still, until finally a temperature of 200° C. is reached. Oil and water distil over into a graduated slanting glass tube 27 in. long, and separate out into two layers. The volume of water is then read off. To prevent boiling over add **toluene** to the crude tar.

Pitch is tested for its *softening* or melting point.

Soft pitch softens at 40° C., melts at 60° C.; medium pitch softens at 60° C., melts at 100° C.; hard pitch softens at 100° C., melts at 150°-200° C.

A rod of soft pitch, $4 \times 4 \times \frac{3}{4}$ in., suitable for making patent fuel, will bend without breaking on heating in water at 60° C. for two minutes. Its **torsional value** is tested by special methods.

The amount of "**Free Carbon**" and "**Bitumen**" in pitch is estimated by boiling the pitch in a flask with a reflux condenser in succession twice each with benzene, carbon disulphide, and alcohol. The residue represents the "free carbon," the difference being the "bitumen."

To *distinguish* **coal-tar** pitch from *natural* asphalt, heat a sample in a crucible. Coal-tar pitch evolves *acrid* fumes, but natural asphalt (usually) a pleasant, bituminous smell.

Recovery of Pyridine Bases from the Distillation Products of Coal-tar

We have described how the various fractions of oil distilled from coal-tar are first washed with sulphuric acid, which abstracts the volatile bases contained in them.

Crude "pyridine-sulphuric acid," from washing the light oils with sulphuric acid, is a brownish liquid, sp. gr. 1.2-1.3, contains 15-20 per cent. of **bases** boiling between 100° and 200° C. Half of these bases is **pyridine**, the rest being the picolines, lutidines, etc.

Pyridine is separated from "pyridine-sulphuric acid" by passing in ammonia gas until a sample of the exit gas smells of pyridine. The liquid separates into two layers, the top one consisting of muddy impurities, the bottom being a solution of pyridine-ammonium sulphate. The bottom layer is run off and completely saturated with ammonia. Pyridine separates as an oil. It is drawn off and fractionated.

Pure pyridine is principally used for denaturing spirits in Germany.

Quinoline is separated in a similar manner from the sulphuric acid washings of the heavier coal-tar Oils. It is used for making the quinoline dyes.

Quinoline (on account of its high boiling point) does not occur largely in the acid washings from crude **benzol**, but is contained, together with acridine and other bases, in the crude sulphuric acid washings from the higher boiling tar oils.

Bone Tar or Bone Oil is the dark evil-smelling liquid formed during the dry distillation of bones in the preparation of bone black (animal charcoal). It contains considerable amounts of pyridine and quinoline, their homologues and other bases. These compounds may be extracted from it by the use of sulphuric acid, and separated as described above.

COAL-TAR PRODUCTS (see Table)

Distillation Products

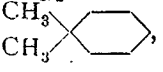
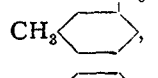
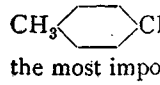
Benzol (Benzene), C_6H_6.—Colourless, mobile liquid, B.P. 80.5°; M.P. 6° C; sp. gr. $\frac{18}{4} = 0.839$. Freezes to white crystals at 0° C. Distinguishable from light petroleum by (*a*) completely dissolving in fuming H_2SO_4 (petroleum does not); (*b*) easily dissolves picric acid and pitch (petroleum does not easily).

FAMILY TREE OF THE COAL-T PRODUCTS
Benzene
Aniline
Fuchsine
Nitrobenzene
Resorcine
Benzene (Toluene
Light Tar
Benzaldehyde
Naphthalene
Phenol, Naph
Phthalic Acid
Anthraquinone
Pitch Anthracene
Heavy Tar Oil
PIT

Valuation.—It should give no blue colour when shaken with concentrated H_2SO_4, and a fragment of isatin (thiophene); should not darken much when shaken with concentrated H_2SO_4 (unsaturated hydrocarbons or thiophene). No unnitrated hydrocarbon should be obtained on treatment with nitro-sulphuric acid and distillation with steam. "*Crude* benzol" is a mixture of benzene, toluene, xylene, etc., and is known as 30 per cent., 50 per cent., or 90 per cent. benzol, according as 30 per cent., 50 per cent., or 90 per cent. of the whole distils over before the thermometer reaches 100° C. Refined benzol should completely distil within half a degree Centigrade.

Toluol (Toluene), $C_6H_5.CH_3$.—Colourless liquid, freezes below −20° C.; B.P. 111° C.; sp. gr. $\frac{15}{4}$ = 0.8708.

Valuation.—Should only slightly darken on shaking with concentrated H_2SO_4.

Xylene, Xyol, $C_6H_4(CH_3)_2$.—Three isomers occur in coal-tar xylene, viz., 2-15 per cent. of **orthoxylene**,  , B.P. 142°; 70-87 per cent. of **metaxylene**,  , B.P. 139°, sp. gr. (19° C.) = 0.8668; 3-10 per cent. **paraxylene**,  , B.P. 138°, M.P. 15° C., sp. gr. 0.8621. **Metaxylene** is technically the most important.

Valuation.—Commercial xylol should distil between 135° and 140° C., and should only turn light brown when shaken with H_2SO_4.

Naphthalene, $C_{10}H_8$ (for preparation from coal-tar see preceding section, p. 418).—Colourless crystalline solid; M.P. 80.5°; B.P. 218° C.; sp. gr. (15° C.) = 1.1517. Sublimes when warmed.

Valuation.—No residue or colour change should be produced when sublimed in air; should melt and boil sharply; should produce no red colour with hot concentrated H_2SO_4, and when solution is diluted with water, filtered, and made alkaline, no smell of pyridine should be apparent. Boiling caustic soda should extract no phenol; should not melt below 79.5° C.

Uses.—See p. 432. Starting point for the production of synthetic indigo (see p. 460).

Anthracene, $C_{14}H_{10}$ (for preparation from **coal-tar** see p. 419).—Colourless crystalline plates with violet fluorescence (when pure); M.P. 213° C.; B.P. just over 360° C. Oxidised, produces **anthraquinone** (which gives with warm NaOH solution and zinc dust a red colour), and with picric acid in **benzene** gives red crystals, M.P. 170° C., of the picrate, $C_{14}H_{10}.C_6H_2.(NO_2)_3.OH$.

To estimate the anthracene in the commercial product, oxidise into anthraquinone by boiling 1 g. for two hours with 45 g. glacial acetic acid to which are slowly added 15 g. of chromic acid dissolved in 10 c.c. of water, leave for twenty-four hours, add 400 c.c. water, stand two hours, filter off anthraquinone, wash with cold water, with boiling NaOH solution, with boiling water, dry in porcelain dish at 100°, heat ten minutes to 100° with 10 g. slightly fuming sulphuric acid, leave twelve hours in a damp place, pour into 200 c.c. cold water, filter off precipitate, wash with alkaline water and with hot water, transfer to dish, dry, *weigh*. Then heat dish until the anthraquinone has volatilised, and *weigh*. Loss of weight = anthraquinone. This multiplied by 85.6 gives percentage of anthracene in sample (see Luck, "Ber.," 6, 1347). It may amount to anything between 30 and 90 per cent., the rest being phenanthrene, carbazol, chrysene, etc.

Uses—Source of valuable dyes. See p. 451.

Phenol (Carbolic Acid), $C_6H_5.OH$.—White crystalline solid, M.P. 41°; B.P. 188° C.; sp. gr. (40° C.) = 1.05433. Commercial samples should melt about 39-40° C., boil about 183°-186° C., and dissolve completely in aqueous caustic soda.

Estimation by titration with standard bromine water. On account of the fact that phenol is extensively used for making picric acid and other explosives, the price in war time invariably rises enormously, and it then becomes profitable to make it from benzol by sulphonating and fusing with NaOH or KOH.

Cresol (Cresylic Acid), $C_6H_4(CH_3).OH$.—Three isomers occur in coal-tar, namely, ortho-, para-, and meta-cresol.

Halogen Derivatives

Benzyl Chloride, $C_6H_5.CH_2Cl$.—Prepared by leading chlorine over the surface of boiling toluene (placed in a sandstone vessel and heated by lead-coated steam pipes) until it has increased in weight by 38 per cent., washing with water, and fractionally distilling: $C_6H_5.CH_3 + Cl_2 = C_6H_5.CH_2Cl + HCl$. Colourless liquid, B.P. 178°; sp. gr. (14° C.) = 1.107. An estimate of the amount of benzotrichloride in it is obtained by observing the amount of green colouring matter produced on heating with dimethylaniline and zinc chloride.

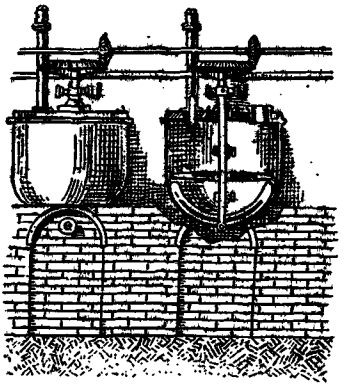


FIG. 195.—Nitrating Apparatus for Nitro-Benzene.

Benzal Chloride, $C_6H_5.CHCl_2$ (Benzylidene dichloride), and **Benzotrichloride**, $C_6H_5.CCl_3$, are simultaneously produced by the further chlorination of boiling toluene, and produce benzaldehyde and benzoic acid when heated with milk of lime. They are not usually separated.

Nitro Compounds (see pp. 632-634)

Nitro-benzene, $C_6H_5.NO_2$, is a light yellow liquid, smelling like bitter almonds, B.P. 207° C.; sp. gr. (15° C.) = 1.208. Is a very good solvent for other nitro compounds including guncotton, etc.

Preparation.—100 kg. benzol are placed in a cast-iron, round-bottomed vessel, fitted with a cover and stirring apparatus, and provided with a condensing tube and an opening for the addition of acid (both placed in the cover), while a tube at the bottom allows the contents to be emptied. A mixture of 115 kg. concentrated nitric acid, sp. gr. 1.38, and 180 kg. concentrated H_2SO_4 are now slowly run in, while the stirrers (lubricated with nitro-benzene) are kept in rapid movement, and the temperature of the whole kept below 25° C. by a stream of cold water flowing round the vessels; when the greater part of the acid has been added, the temperature is allowed to increase to 50° C. The following action has taken place:—

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitro-benzene.}}{C_6H_5.NO_2} + \underset{\text{Water.}}{H_2O}$$

The acid is run into the benzene (thereby keeping the latter in excess until the last), and the temperature is kept low in order to avoid the second reaction:—

$$\underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Di-nitro-benzene.}}{C_6H_4(NO_2)_2} + \underset{\text{Water}}{H_2O}$$

The stirring and cooling apparatus must be efficient, as the nitrating mixture is otherwise liable to spontaneously inflame.

After all the acid has been slowly added the stirring is continued for some

hours until no more action takes place. The whole is allowed to stand, and the **nitro-benzene** separates as an oil on the surface of the acid.

The acid is run off at the bottom. It contains about 1 per cent. of nitric acid, water, and organic compounds. It is "regenerated" for use by allowing it to slowly flow, cascade fashion, down a series of six porcelain vessels, heated in a stream of hot air.

During the heating the water and nitric acid vaporises (the nitrous fumes being condensed and used in the manufacture of nitric acid), and there finally flows out of the last vessel concentrated sulphuric acid, 66° Bé., which is used again for nitrating.

After the acid has been drawn off, the nitro-benzene is then run into large wooden vessels, and washed with water until all traces of acid are removed.

When required quite pure (for perfumery) it must be steam distilled. Usually any unused benzene present is first removed by blowing steam through the mixture, and the nitro-benzene coming over with the benzene is used again for nitrating.

For making dyes, etc., it is usually unnecessary to distil the benzol.

Yield.—100 parts of benzene give 150-152 parts nitro-benzene.

Metadinitrobenzene, $C_6H_4(NO_2)_2$.—Crystalline needles, M.P. 89.9° C. It is prepared in the apparatus used for making **nitro-benzene**, using stronger acids.

To 100 kg. benzene, 200 kg. nitric acid (40° Bé.) and 300 kg. concentrated sulphuric acid (66° Bé.), previously mixed together, are allowed to flow in, and after the action is over, the contents of the pot are withdrawn while still hot, the dinitrobenzol allowed to solidify, and purified by crystallisation. It is used for making diaminobenzene and explosives (see p. 634).

For **Trinitrobenzene** see p. 634.

Ortho- and Paranitrophenol, $C_6H_4NO_2.OH$.—1 part of phenol is mixed with a little water, and then a mixture of 2 parts nitric acid (sp. gr. 1.38) and 4 parts of water is gradually added, cooling the liquid the whole time. After the reaction is completed the oil is washed with water and the *o*-nitrophenol steam distilled over, the paranitrophenol remaining behind.

Trinitrophenol, Picric Acid, $C_6H_2(NO_2)_3.OH$, is made by heating phenol sulphonic acid with nitric acid. For details see p. 632. Used as an explosive. For use as dye, see p. 479.

Mono Nitrotoluenes.—Three isomerides are known, viz.:—

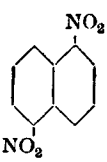
	Melting Point.	Boiling Point.
Orthonitrotoluene	Liquid.	218°-219° C.
Metanitrotoluene	16° C.	230°-231° C.
Paranitrotoluene	54° C.	234° C.

Under ordinary conditions of nitrating, ortho- and paranitrotoluene are principally produced, and may be separated (when necessary) by fractionally distilling under diminished pressure.

Mixtures of nitro-benzene and nitrotoluene and nitroxylene, $C_6H_3(CH_3)_2.NO_2$, are also prepared; also nitro-benzylchloride, $C_6H_4(NO_2).CH_2Cl$; nitro-benzaldehyde chloride, $C_6H_4(NO_2).CHCl_2$, mono-nitronaphthalene, etc. etc.

Dinitrotoluene, $C_6H_3(CH_3).(NO_2)_2$, is prepared in much the same way as dinitrobenzene (see p. 364).

The **Trinitrotoluenes** are used as explosives. See pp. 633, 634.



α_1-α_2-Dinitronaphthalene.

α_1-α_2-**Dinitronaphthalene** is used for making explosives, alizarin black, and diaminonaphthalene. **Naphthalene** is allowed to stand twenty-four hours in contact with strong nitric acid, sulphuric acid is added, and the mixture heated twelve to twenty-four hours on the water bath, the product washed with water, and extracted in succession with carbon disulphide and acetone, in order to eliminate as much as possible the other isomerides formed at the same time. The pure product melts at 217° C. (see p. 334).

Bases

Aniline, $C_6H_5.NH_2$, is prepared on a very large scale by reducing nitro-benzene with **iron** and **hydrochloric acid.**

500 parts of nitro-benzene and 800 parts of water are placed in a large iron still provided with a mechanical agitator and condenser, and the whole is heated to boiling by blowing in steam. 16-20 parts of hydrochloric acid are now added, the steam is shut off, and 550 parts of finely ground cast-iron borings are gradually added during about eight hours. A vigorous action takes place, heat is evolved, and a mixture of water, aniline, and nitro-benzene distil over in a steady stream, and are continually returned to the still.

Great care must be taken in adding iron not to let the action become too violent, since violent explosions have been known to occur.

The following actions take place :—

$$\underset{\text{Nitro-benzene.}}{C_6H_5.NO_2} + \underset{\text{Iron.}}{3Fe} + \underset{\substack{\text{Hydro-}\\\text{chloric acid.}}}{6HCl} = \underset{\text{Aniline.}}{C_6H_5.NH_2} + \underset{\substack{\text{Ferrous}\\\text{chloride.}}}{3FeCl_2} + \underset{\text{Water.}}{2H_2O}.$$

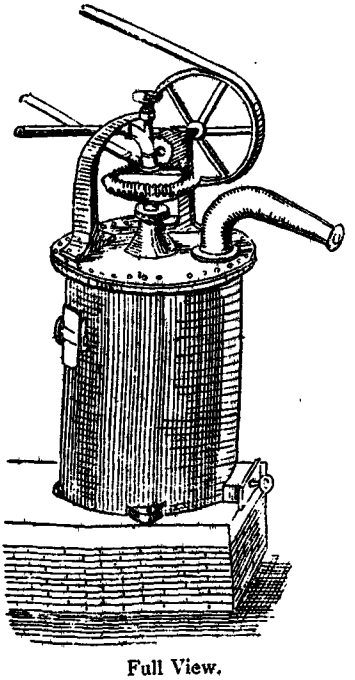
$$C_6H_5NO_2 + 2Fe + H_2O = C_6H_5NH_2 + Fe_2O_3.$$

$$Fe + 4Fe_2O_3 = 3Fe_3O_4.$$

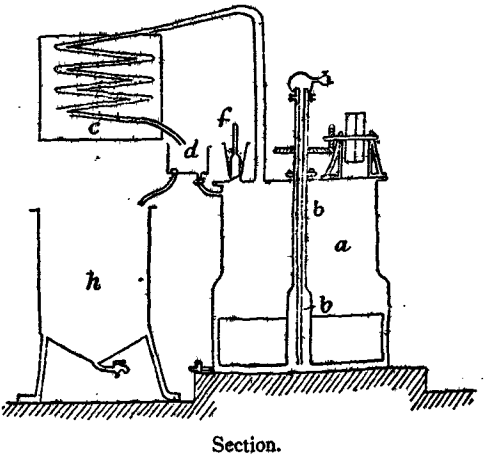
According to the first equation 178 parts of HCl are required for the reduction of 100 parts of nitro-benzene.

In practice 9 parts of HCl are sufficient, in consequence of the reaction largely proceeding according to the second equation.

When all the iron has been added the heating is continued by steam, and the distillate returned so long as it is yellow (presence of nitro-benzene). When the distillate comes over colourless, it is collected in *h* (Fig. 196), and the distillation continued so long as aniline comes over. The aniline collects in a layer at the bottom and is drawn off from time to time. The



Full View.



Section.

FIG. 196.—Reducing Apparatus for Nitro-Benzene.
Steam is blown in through the hollow shaft of the stirrers.

water condensed from the steam distillation contains up to 3 per cent. dissolved aniline and toluidine, and is returned again to the boiler and used for another aniline distillation. The aniline thus obtained is purified by redistillation in special stills.

The residue in the still consists of metallic iron, and oxides and chlorides of iron, mixed with tarry impurities. Sometimes it is smelted for iron in iron-works, often it is worked up into green vitriol (iron sulphate). If allowed to accumulate the spontaneous oxidation of the finely divided iron may cause the mass to become incandescent.

Yield.—100 parts nitro-benzene give 70 aniline.

Properties.—Colourless oil, B.P. 182°; M.P. 8°; sp. gr. (15° C.) = 1.0275. Soluble in 32 parts of water at 15° C. Completely soluble in acids.

Tests.—Aniline water gives a violet colour with bleaching powder solution. It may be estimated by titrating with sodium nitrite solution. The presence of benzene or nitro-benzene, etc., in aniline is detected by their insolubility in acids.

Aniline for Red is a mixture of aniline with both toluidines, *e.g.*, 33.3 per cent. aniline, 28 per cent. paratoluidine, 42.7 per cent. *o*-toluidine, sp. gr. 1.008 at 15° C.; B.P. 190-198.

Aniline for Safranine consists of aniline (40 per cent.) and *o*-toluidine (60 per cent.).

"**Aniline for Blue**" or "light aniline" is aniline free from toluidine, 80 per cent. of which distils between 182°-182.5°. It is used for phenylating rosaniline. See under **Rosaniline Blue.**

Toluidine, $C_6H_4(CH_3)NH_2$ (ortho-, meta-, and para-), and

Xylidine, $C_6H_3(CH_3)_2NH_2$, and other similar bases are prepared in much the same way as aniline by reducing the corresponding nitro compounds.

Dimethylaniline, $C_6H_5.N(CH_3)_2$, is prepared by heating a mixture of aniline (75 parts), aniline hydrochloride (25 parts), and methyl alcohol (free from acetone) in a cast-iron autoclave (see Fig. 197) to 230°-270° C., and rectifying the product:—

$$C_6H_5.NH_2.HCl + 2CH_3OH = C_6H_5.N.(CH_3)_2 + HCl + 2H_2O$$
$$HCl + C_6H_5NH_2 = C_6H_5.NH_2.HCl.$$

Colourless oil; B.P. 192°; sp. gr. (15° C.) = 0.976. Used for making methylene blue, indophenol, malachite green, etc.

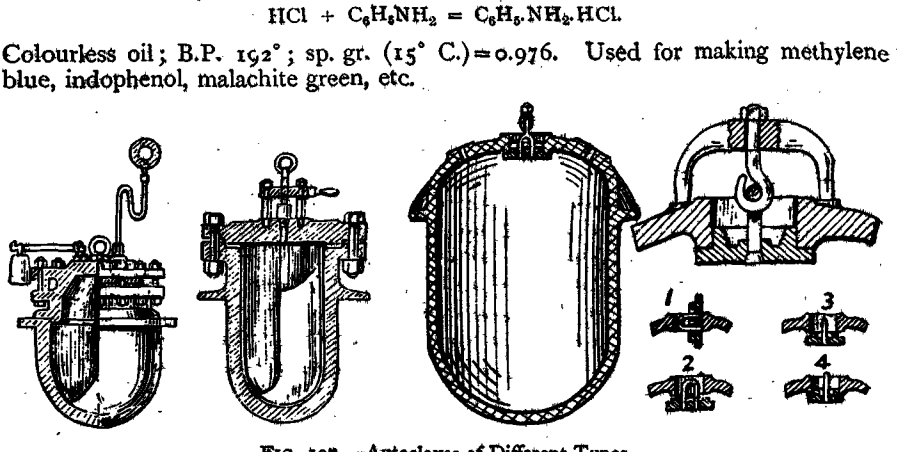


FIG. 197.—Autoclaves of Different Types.
1, 2, 3, 4 shows method of inserting stopper.

By treating the product (26 kg.) with HCl (100 kg. of 31 per cent. HCl), stirring, adding chopped ice (100 kg.) and then sodium nitrite (16 kg. in 351 kg. H_2O) we get *p*-nitroso-dimethyl-aniline as an oil :—

$$C_6H_5.N.(CH_3)_2 + HNO_2 = C_6H_4\begin{cases}NO\\N.(CH_3)_2\end{cases} + H_2O.$$

Dimethylaniline. Nitrous acid. *p*-Nitroso-dimethylaniline. Water.

Used for making various dyes.

Diphenylamine, $(C_6H_5)_2.NH$, is prepared by heating molecular proportions of aniline and aniline hydrochloride together in an autoclave for some hours at 200° C., boiling with dilute HCl to remove aniline, and distilling the residual oil, which is diphenylamine. Forms monoclinic plates; M.P. 54° C.; B.P. 310°.

The **Phenylenediamines**, $C_6H_4(NH_2)_2$.—All three varieties are in use :—

	M.P.	B.P.
Orthophenylenediamine	102° C.	252° C.
Metaphenylenediamine	63° C.	287° C.
Paraphenylenediamine	147° C.	267° C.

m-Phenylenediamine is prepared by reducing *m*-dinitro-benzene with iron and hydrochloric acid.

200 parts of *m*-dinitro-benzene and 200 parts of water are placed in a large iron vessel provided with a mechanical agitator and condenser (see under **Aniline**, Fig. 196). Steam is blown until the mixture boils, then 16 parts of hydrochloric acid are run in and 430 parts of finely ground cast-iron borings are slowly added; when the action is complete the liquid is made alkaline with sodium carbonate, and boiled up with 800-1,000 parts of water, the liquid filtered from the iron sludge (which is again extracted with water) and the solution of the *m*-phenylenediamine either used directly for making substances like Bismarck brown, or it may be neutralised with hydrochloric acid, evaporated, and obtained as hydrochloride. On adding concentrated NaOH solution to the concentrated hydrochloride solution, the base is set free as an oil, which, rising to the surface, solidifies on cooling, and is purified by distillation.

Colourless solid; M.P. 83° C.; B.P. 287. Soluble in water.

p-**Phenylenediamine** is prepared by reducing *p*-nitraniline with iron and hydrochloric acid.

Benzidine, $\begin{matrix}C_6H_4.NH_2\ (1:4)\\C_6H_4.NH_2\ (1:4)\end{matrix}$, is prepared by reducing nitro-benzene with zinc dust and caustic soda in an iron vessel provided with a powerful stirrer. Any aniline formed is distilled off with steam, and the product run out and treated with cold dilute hydrochloric acid to dissolve out zinc hydrate. There is thus left hydrazobenzene, $C_6H_5.NH.NH.C_6H_5$:—$Zn + 2NaOH = Zn(ONa)_2 + 2H$

$$C_6H_5.NO_2 + C_6H_5.NO_2 + 10H = C_6H_5.NH - NH - C_6H_5 + 4H_2O.$$

This is converted into **benzidine** (by intramolecular change) thus :—

$$C_6H_5.NH.NH.C_6H_5 = NH_2.C_6H_4.C_6H_4.NH_2$$

by boiling with hydrochloric acid, filtering, and precipitating the base as sulphate by sulphuric acid or sodium sulphate. The base may be obtained by decomposing the sulphate by caustic soda and distilling. Crystalline plates; M.P. 122°; B.P. above 360° C. Nitrous acid converts it into tetrazodiphenyl $\begin{matrix}C_6H_4-N:N.OH\\C_6H_4.N:N.OH\end{matrix}$ which combines with sulphonic acids of phenols and amines to form azo colours, such as Congo, Chrysamine, which dye cotton from an alkaline bath without a mordant. See **Synthetic Dyes**.

Nitraniline, $C_6H_4.NO_2NH_2$.—Of the three varieties the meta and para compounds are chiefly used in colour manufacture. **Metanitraniline** is prepared by the partial reduction of dinitro-benzene with iron and hydrochloric acid, or with ammonium sulphide; also from finely powdered aniline nitrate, by adding it, in a finely powdered condition, into concentrated sulphuric acid (cooled to $-5°$ C.), stirring, pouring into 400 l. water, and decomposing with caustic soda; yellow prisms, M.P. 114° C.

Paranitraniline is prepared from *p*-nitracetanilide (see Nölting and Collin, "Ber.," 17, 262) by warming with dilute sulphuric acid; yellow prisms, M.P. 147° C.

Amidophenol, $C_6H_4.NH_2.OH$.—The ortho-amidophenol is obtained by mixing 50 parts of *o*-nitrophenol with 300 parts of ammonia and reducing by passing in H_2S. Meta-amidophenol is obtained by reducing *m*-nitrophenol, or by heating resorcinol with ammonia; para-amidophenol is obtained by reducing *p*-nitrophenol.

α-Naphthylamines, $C_{10}H_7.NH_2$, is manufactured by reducing α-nitronaphthalene with iron and hydrochloric acid, as in the case of aniline.

800 kg. iron borings and 40 kg. hydrochloric acid are mixed, with the addition of some water, in a large vessel provided with a powerful stirring apparatus. The warmed mixture has then added to it in small portions about 600 kg. nitronaphthalene, and the reduction proceeds vigorously, continually stirring the whole time. The nitronaphthalene must be added at such a rate that the internal temperature is maintained about 50° C. Finally the mixture is, after the reaction has ceased, stirred vigorously for six to eight hours, while the temperature is maintained at about 50°-70° C. by blowing in steam. Samples are withdrawn from time to time, and the unchanged nitronaphthalene estimated (by distilling and dissolving the product in HCl). Finally milk of lime is added (about 50 kg.), the mixture vigorously stirred, and the vessel emptied. The following reaction takes place (Witt):—

$$24Fe_2Cl_2 + 4C_{10}H_7NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_{10}H_7NH_2;$$
$$12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2.$$

The crude naphthylamine is now distilled from box-shaped iron retorts, through which a stream of superheated steam is driven to facilitate distillation, the condensing worms being kept at 60° C. by immersion in hot water in order to prevent them from being choked by crystallising naphthylamine.

The α-naphthylamine is obtained pure by a single redistillation. *Flat* needles or plates with an unpleasant smell—M.P. 50° C.; B.P. 300° C.

β-Naphthylamine, $C_{10}H_7.NH_2$, is prepared by heating 10 kg. β-naphthol, 4 kg. NaOH, and 4 kg. NH_4Cl in an autoclave for sixty to seventy hours at 150°-160° C.—M.P. 112° C.; B.P. 294.

***m*-Aminophenol**, $C_6H_4(OH).NH_2$, is manufactured by heating 20 kg. NaOH with 4 kg. water in an autoclave to 270° C., and then adding 10 kg. *m*-aminobenzolsulphonic acid, $C_6H_4.SO_3H.NH_2$, and heating at 280°-290° C. for one hour, when the sodium salt of the base is produced thus:—

$$C_6H_4\begin{cases}SO_3Na\\NH_2\end{cases} + Na_2O = C_6H_4\begin{cases}ONa\\NH_2\end{cases} + Na_2SO_3$$

The base, *m*-aminophenol, may be obtained by decomposing the sodium salt with acid or carbon dioxide.

***m*-Oxydimethylaniline**, $C_6H_4\begin{cases}OH\\N.(CH_3)_2\end{cases}$, is prepared in a similar manner from the sulphonic acid of dimethylaniline.

Aminonaphthol, $C_{10}H_6\langle^{OH}_{NH_2}$, is likewise prepared by fusing naphthylamine-sulphonic acid, $C_{10}H_6\cdot\langle^{SO_3H}_{NH_2}$, with caustic soda.

Pyridine, C_5H_5N, is obtained from the sulphuric acid washings of light benzol as described p. 420, also from **bone tar** or **bone oil** (obtained during the dry distillation of bones for animal charcoal). Colourless mobile oil, of unpleasant smell, B.P. 116.7° C.; sp. gr. (0° C.) = 0.9858.

Quinoline, C_9H_7N, is an oily liquid, B.P. 238° C.; sp. gr. (20° C.) = 1.094; occurs in the coal-tar and bone-oil bases. It is prepared by heating aniline (216 parts) and glycerol (600 parts) with concentrated sulphuric acid (600 parts) and nitro-benzene (144 parts) for one day at 125° C., then at 180°-200° C. until reaction is complete.

The glycerol decomposes thus:—

$$\underset{\text{Glycerol.}}{C_3H_8O_3} - \underset{\text{Water.}}{2H_2O} = \underset{\text{Acrolein.}}{CH_2 : CH.CHO}$$

and the acrolein combines with the aniline thus:—

$$\underset{\text{Aniline.}}{C_6H_5.NH_2} + \underset{\text{Acrolein.}}{C_3H_4O} + \underset{\substack{\text{Oxygen}\\ \text{from the}\\ \text{nitro-benzene.}}}{O} = .C_9H_7N + 2H_2O.$$

The mixture is diluted with water, excess of nitro-benzene boiled off, the base set free by soda, the quinoline is distilled, purified from aniline by treating in acid solution with $K_2Cr_2O_7$ or $NaNO_2$. Yield, 70 per cent.

The *quinoline* of commerce, usually obtained from the basic portions of coal-tar oils, contains **quinaldine**, $C_{10}H_9N$, and isoquinoline, C_9H_7N. The former may be prepared in a similar manner by heating aniline and aldehyde, or paraldehyde with dehydrating agents, such as aluminium chloride and hydrochloric acid.

Acridin, $C_{13}H_9N$, a derivative of anthracene, is a crystalline body produced by treating diphenylamine, $C_6H_5.NH.C_6H_5$, and formic acid, H.COOH, with zinc chloride. Also obtained, along with quinoline, from the sulphuric acid washings of the heavier coal-tar oils.

Phenylhydrazine, $C_6H_5.NH.NH_2$. — 10 parts aniline are dissolved in 200 parts concentrated HCl, the liquid cooled, and 7.5 parts of sodium nitrite, dissolved in 50 parts water, are gradually added. Diazobenzene chloride is formed. thus:—

$$C_6H_5.NH_2.HCl + NaNO_2 + HCl = C_6H_5 - N = N - Cl + NaCl + 2H_2O.$$

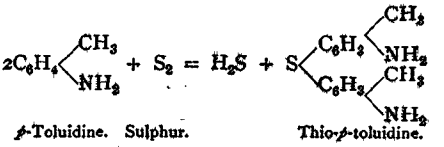
The solution is then neutralised and reduced by adding neutral potassium sulphite and acid metasulphite:—

$$C_6H_5.N_2.Cl + K_2SO_3 = C_6H_5.N_2.SO_3K + KCl.$$
$$C_6H_5.N_2.SO_3K + KHSO_3 + H_2O = C_6H_5.NH.NH.SO_3K + KHSO_4.$$

The phenylhydrazine-*p*-sulphonic acid, $C_6H_5.NH.NH.SO_3H$, thus obtained is used directly thus in the colour industry. If the base itself is required (for manufacturing antipyrene), the solution is boiled with concentrated HCl, when the chlorhydrate $C_6H_5.NH.NH_2.HCl$, is obtained, and from this the base may be set free by adding alkalki. When quite pure forms crystals, M.P. 23° C. As usually obtained it is an oil, B.P. 241°-242° C.

Sulphur Bases

When *p*-toluidine is heated with sulphur at 140° C. in the presence of lead oxide, **Thiotoluidine** is obtained (Merz and Werth, *Ber.*, 4, 393), thus:—



p-Toluidine. Sulphur. Thio-*p*-toluidine.

The bases crystallise from alcohol in colourless, odourless plates, and unite with two molecules of HCl, thus:—$C_{14}H_{16}N_2S,2HCl$. If *p*-toluidine is heated with more sulphur to a higher temperature (eighteen hours at 180°-190° C. and six hours at 200°-220°), **Toluthiazol** is obtained:—

p-Toluidine. Toluthiazol.

and has the constitution

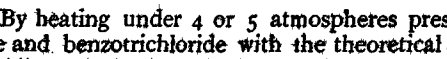
This is not a dyestuff, but if a higher temperature and more sulphur be employed in its preparation, a base is formed which on sulphonation yields **Primuline Yellow.**

A large and important class of sulphur colours are derived from these and similar bases, which are now rapidly increasing in value.

Aldehydes

Benzaldehyde (bitter almond oil), $C_6H_5.CHO$.

Preparation.—(1) By heating under 4 or 5 atmospheres pressure a mixture of benzylidene dichloride and benzotrichloride with the theoretical amount of caustic soda or lime, and distilling off the benzaldehyde with steam. Sodium or calcium benzoate remains behind:—



Benzal chloride. Caustic soda. Benzaldehyde. Water.

Small quantities of chlorine compounds are contained in benzaldehyde prepared in this way. This does not matter for the colour industry, but if the benzaldehyde is to be used for perfuming purposes, it loses greatly in value, and now is successfully prepared for this purpose (2) by oxidising toluene with nickel or cobalt oxide (German Patent, 306,071, 1901; *Chemiker Zeitung*, 25, 439, 1901).

Colourless liquid with smell of bitter almonds, B.P. 180° C.; sp. gr. (15° C.) = 1.0504.

Valuation.—90 per cent. of commercial product should distil between 177° C. and 181° C.; should have sp. gr. at 15° C. = 1.0504; 1 volume should dissolve almost completely in 10 volumes warm aqueous sodium bisulphite, sp. gr. 1.11, and on extracting solution with ether, evaporating ether, no pungent-smelling residue should be left (benzyl chloride). Chlorine is detected by fusing with sodium hydrate and nitrate, and precipitating with silver nitrate. Adulteration with nitro-benzene is detected by a *green* colour on heating with strong potash solution, also by presence of N (heating with Na). On long keeping it oxidises to benzoic acid which crystallises out.

Carboxylic Acids

Benzoic Acid, $C_6H_5.COOH$, is prepared from the calcium or sodium benzoate left in the preparation of benzaldehyde (see above); after distilling off all the benzaldehyde the calcium benzoate is decomposed by hydrochloric acid, the precipitated benzoic acid is filtered off, dried, and sublimed. White needles, M.P. 121° C.; B.P. 249° C. Soluble in boiling water.

Salicylic Acid, $C_6H_4(OH).CO_2H$, is prepared by submitting dry sodium phenate (from phenol and caustic soda) to the action of dry carbon dioxide gas at ordinary temperatures, when sodium phenyl carbonate is formed:—

$$C_6H_5.ONa + CO_2 = C_6H_5O.CO_2.Na.$$

This is then heated in a closed vessel at 120°-130° C. for several hours, when it is converted quantitatively into **sodium salicylate**—

$$\left(C_6H_5.O.CO_2.Na = C_6H_4\begin{matrix}OH\\COONa\end{matrix}\right),$$

which is dissolved in water and salicylic acid precipitated by adding hydrochloric acid. White needles, M.P. 156°. Steam-volatile. Sparingly soluble in cold water. Gives a violet coloration with ferric chloride.

The manufacture and decolorisation are difficult. For details see D.R. Patents, 429, 29,939, 38,742, 65,131, 67,893, 73,279, 78,708, 133,500; also see Rautert, *Ber.*, 1875, 8, 537; Henderson. *Journ. Soc. Chem. Ind.*, 1890, 9, 591.

Phthalic Acid (*o*-benzenedicarboxylic acid, $C_6H_4.(CO_2H)_2$ (1 : 2).

Preparation.—100 parts naphthalene, 1,500 parts concentrated sulphuric acid, 50 parts mercury are heated together until the naphthalene is dissolved; then the mass is heated to 300° C. in a still, when sulphur dioxide, carbon dioxide, water, phthalic acid, and phthalic anhydride distil over. On cooling the crystals of phthalic acid are separated and dried by the centrifugal machine.

When heated with ammonia it yields **phthalimide**, $C_6H_4\begin{matrix}CO\\CO\end{matrix}NH$.

Plates, M.P. 213° C.; sparingly soluble in cold water, insoluble in chloroform.

The **anhydride**, $C_6H_4\begin{matrix}CO\\CO\end{matrix}O$, forms long white needles, M.P. 128° C.; B.P. 284° C. Largely used as a raw material for anthranilic acid, and so for synthetic indigo.

Anthranilic Acid (*o*-aminobenzoic acid), $C_6H_4(NH_2).CO_2H$, is prepared by dissolving 1 part phthalimide and 2 parts NaOH in 7 parts water, cooling, and gradually stirring in 10 parts of sodium hypochlorite solution (5 per cent. NaOCl); finally heating to 80° C. for some minutes, cooling, neutralising, and adding acetic acid in excess, when the greater part of the anthranilic acid separates out:—

$$C_6H_4\begin{matrix}CO\\CO\end{matrix}NH + NaOCl + 3NaOH = C_6H_4\begin{matrix}NH_2\\COONa\end{matrix} + Na_2CO_3 + NaCl + H_2O.$$

The anthranilic acid still remaining in solution is precipitated in the form of a copper salt by adding copper acetate. Can also be easily prepared from *o*-chlorbenzoic acid, $C_6H_4.Cl.COOH$ (1 : 2), by heating with NH_3 in the presence of a trace of copper. (In the absence of copper no action takes place.) Colourless plates, M.P. 145° C. Used for manufacturing artificial indigo (see p. 460).

Diazo Compounds

LITERATURE

CAIN.—"Chemistry of the Diazo Compounds." London, 1908.
See also under **Synthetic Dyes.**

When a solution of sodium nitrite is added to a solution of a primary amine (containing the group NH_2), and the mixture is acidified, "Diazo Compounds," containing the group, —N=N—, are formed, which are usually unstable and sometimes explosive, but nevertheless give rise to a large number of valuable colouring matters.

Diazobenzene chloride, C_6H_5—N=N—Cl, one of the most frequently used

diazo compounds, is only known in solution, and is obtained by "diazotising" aniline hydrochloride according to the following equation:—

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5.NH_2.HCl} + \underset{\text{Sodium nitrite.}}{NaNO_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Diazobenzene chloride.}}{C_6H_5{-}N{=}N{-}Cl} + \underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Water.}}{2H_2O}$$

The solution of aniline hydrochloride is cooled by adding ice, and a 10 per cent. solution (accurately titrated) of sodium nitrite gradually run in, in the exact amount required to decompose the base, excess of nitrous acid being avoided (*test*: free nitrous acid turns KI + starch paper blue). The diazobenzene chloride is then immediately used while still in a liquid form.

Similarly **Diazobenzene nitrate**, $C_6H_5{-}N{=}N{-}NO_3$, may be obtained by diazotising a solution of aniline in nitric acid (aniline nitrate), but although it can be obtained in a crystalline state, is always used in the liquid form, since the solid product is dangerously explosive.

All these diazo compounds are extremely reactive in the liquid form. For example, diazobenzene chloride, when added to aniline, immediately reacts as follows:—

$$\underset{\text{Diazobenzene chloride.}}{C_6H_5{-}N_2{-}Cl} + 2\underset{\text{Aniline.}}{C_6H_5.NH_2} = \underset{\substack{\text{Diazoaminobenzene}\\\text{(Gold yellow dye).}}}{C_6H_5{-}N{=}N{-}NH.C_6H_5} + \underset{\bullet}{C_6H_5.NH_2.HCl}$$

The product, in the presence of aniline salts, may undergo an intramolecular transformation, forming aminoazobenzol: $C_6H_5.N{=}N{-}C_6H_5.NH_2$, which again can be diazotised. Besides monodiazo compounds di-, tri-, tetra-diazo compounds occur, containing two, three, four, and more "diazo groups," —N=N—, and these bodies form an enormous number of colouring matters known as "azo dyes" (*q.v.*).

Sulphonic Acids

This important class of bodies contains the group SO_3H, and, accordingly as this occurs once, twice, or more, are known as mono-, di-, tri-, etc., sulphonic acids. They are, as a class, distinguished by their solubility in water, and thus arises the possibility of using many substances as "dyes" which, unless sulphonated, are insoluble and so useless. They are formed by acting on aromatic compounds with the following three agents:—

1. **Concentrated Sulphuric Acid**, 66° Bé. in the cold.

2. **Fuming Sulphuric Acid**, consisting of SO_3 dissolved in concentrated H_2SO_4.

3. **Chlorsulphonic Acid**, SO_3HCl, prepared by heating together fuming sulphuric acid and salt:—

$$\underset{\substack{\text{Fuming sulphuric}\\\text{acid.}}}{H_2S_2O_7} + NaCl = SO_3HCl + NaHSO_4.$$

In the last named agent, the sulphonation, although proceeding readily, has the disadvantage of being attended with the evolution of HCl gas, thus:—

$$\underset{\substack{\text{Chlorosulphonic}\\\text{acid.}}}{SO_3HCl} + \underset{\text{Benzene.}}{C_6H_6} = \underset{\substack{\text{Benzene sulphonic}\\\text{acid.}}}{C_6H_5.SO_3H} + \underset{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid.}}}{HCl}$$

Benzene-monosulphonic Acid, $C_6H_5.SO_3H + 1\frac{1}{2}H_2O$, is prepared by agitating together 2 parts of benzene and 3 parts fuming sulphuric acid, with gentle warming, until no more benzene is dissolved. Next chalk is added and the liquid filtered from the precipitated calcium sulphate, and concentrated. Needles, M.P. 40°-42° C.; deliquescent.

m- and *p*-**Benzene disulphonic Acid**, $C_6H_4(SO_3H)_2$ (1 : 3) and (1 : 4).—A mixture of both these acids is used for preparing resorcin. 1 part benzene vapour is led into 4 parts concentrated sulphuric acid heated to 240° C. in retorts provided

with reflux condensers. The acid is neutralised with chalk, and the calcium salts crystallised from water, when the meta compound crystallises first. Sometimes the calcium salts are transformed into potassium salts and the isomers separated by crystallisation, the potassium salt of the meta acid being less soluble than that of the para acid.

***p*-Sulphanilic Acid**, $C_6H_4.NH_2.SO_3H$ (1 : 4), is prepared by mixing 100 parts of aniline with 105 parts of concentrated sulphuric acid, and heating on trays in an oven at 180°-220° C. ***m*-Sulphanilic Acid** is prepared by reducing *m*-nitrobenzene-sulphonic acid. Both varieties are colourless, crystalline solids, moderately soluble in water.

Xylidine Sulphonic Acid, $C_6H_2(CH_3)_2NH_2.SO_3H$, is prepared by heating commercial **xylidene** (120 parts) with 400 parts of fuming (20 per cent. SO_3) sulphuric acid, pouring the product into cold water, when the sparingly soluble sulphonic acid of metaxylidene, $C_6H_2.(CH_3)_2.NH_2.SO_3H$ (1 : 3 : 4 : 6), separates out. The mother liquor is converted into sodium salts and concentrated, when sodium *p*-xylidene sulphonate, $C_6H_2(CH_3)_2NH_2.SO_3H$ (1 : 4 : 2 : 5), separates out.

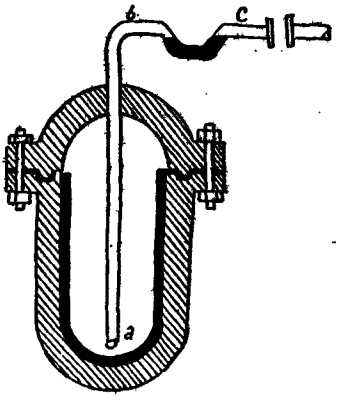


FIG. 198.

Nitrotoluene Sulphonic Acid, $C_6H_3.CH_3.SO_3H.NO_2$, is prepared by dissolving 1 part of *p*-nitrotoluol in 3 parts of fuming sulphuric acid and running the mixture into 15 parts of saturated brine, when the sodium salt of the acid crystallises out.

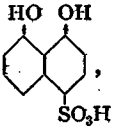
Naphthalene Sulphonic Acids, $C_{10}H_7.SO_3H$.—The α-acid is obtained by treating 1 part finely divided naphthalene with 2 parts concentrated H_2SO_4 or 10-15 per cent. fuming sulphuric acid, keeping the temperature between 20° C. and 40° C. By raising the temperature to 160°-180° C. the β-acid is obtained, and can be separated as a calcium salt.

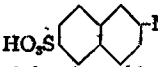
Naphthalene-disulphonic Acid, $C_{10}H_6.(SO_3H)_2$, is obtained by heating 1 part naphthalene with 5 parts concentrated H_2SO_4 for four hours at 160°-180° C., and separating the α- and β-sulphonic acid, produced at the same time, as calcium salts.

Naphthylamine Sulphonic Acid $C_{10}H_6.SO_3H.NH_2$, is prepared by heating naphthalene sulphonic acid with a 20 per cent. ammonia solution in an autoclave under a pressure of 12 atmospheres :—

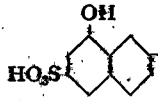
$$C_{10}H_7.SO_3H + NH_3 + H_2O = C_{10}H_6.(SO_3H).NH_2 + H_2 + H_2O.$$

Since hydrogen is formed and may not escape directly into the air (since it forms an explosive mixture with air) a special apparatus is used whereby contact of the hydrogen with air is avoided when the contents are discharged. A long tube *a b c* passes through the cover down nearly but not quite to the bottom of the autoclave, the tube being bent at its upper end *c*, as in Fig. 8, and this part of the bend is filled with water, which prevents access of air to the hydrogen in the boiler. During the reaction the tube is firmly closed. But when the reaction is completed the tube is connected to another tube and the hydrogen pressure in the interior is used to force out the contents through the central tube—only a small residue of liquid finally remaining in the boiler, which is used again for another operation.

$\alpha_1\alpha_4$-Dioxynaphthalene-α_2-sulphonic Acid,  , is produced by melting $\alpha_1\alpha_2\alpha_4$-naphthol disulphonic acid with solid NaOH at 250° C., or with NaOH solution under pressure. White crystals; produces valuable azo dyes.

$\beta_1\beta_3$-Naphthylamine Sulphonic Acid,  , is prepared by heating the ammonium salt of $\beta_1\beta_3$-naphthol sulphonic acid for two days at 180°-200° C. in an autoclave:—

$$C_{10}H_6\begin{matrix}OH\\SO_3.NH_4\end{matrix} = C_{10}H_6\begin{matrix}NH_2\\SO_3H\end{matrix} + H_2O.$$

$\beta_1\alpha_4\beta_3$-Aminonaphthol Sulphonic Acid,  , is produced by melting β-naphthylamine disulphonic acid with NaOH at 185° C. for six hours in an autoclave.

Phenylhydrazine-p-sulphonic Acid, $C_6H_4.(NH.NH_2).SO_3H$ (1:4), is obtained by reducing diazobenzene sulphonic acid (from p-sulphanilic acid) with sodium sulphite and boiling with concentrated HCl. Also by sulphonating phenylhydrazine (which see).

The Phenols (see Phenol, Cresol, p. 422).

Resorcinol, $C_6H_4.(OH)_2$. (1:3), is prepared by heating for eight to nine hours to a temperature of 270° C. 60 kg. of sodium benzene disulphonate with 150 kg. of caustic soda in a cast-iron vessel, provided with mechanical agitation. The product is dissolved in water, acidified, extracted with ether, the ether distilled, and the crude resorcinol so obtained purified by sublimation or crystallisation. Crystalline solid; M.P. 118° C.; B.P. 277° C.

Pyrogallol, $C_6H_3.(OH)_3$. (1:2:3), is prepared by heating gallic acid with three times its weight of water for half an hour at 200°-210° C. in an autoclave. A pad of pappé is inserted round the lid of the cover so that the CO_2 gradually escapes:—

$$\underset{\text{Gallic acid.}}{C_6H_2(OH)_3.COOH} = \underset{\text{Pyrogallol.}}{C_6H_3.(OH)_3} + \underset{\text{dioxide.}}{\underset{\text{Carbon}}{CO_2}}$$

The solution is boiled with animal charcoal, filtered, and evaporated. White needles; M.P. 132° C.; B.P. 210° C.; easily soluble in water. Its solution in alkali rapidly absorbs oxygen from the air.

The Naphthols, $C_{10}H_7.OH$

Two varieties exist: α-naphthol, M.P. 94° C.; β-naphthol, M.P. 122° C. **α-Naphthol** is prepared by fusing sodium α-naphthalene sulphonate (1 part) with 2-3 parts caustic soda and a little water at 270°-300° C. in an iron vessel provided with an agitator. The sodium naphtholate rises to the surface, is separated from the lower layer of caustic soda and sodium sulphite, and decomposed with CO_2 gas. The precipitated naphthol is dried and distilled:— $C_{10}H_7.SO_3H + K_2O = C_{10}H_7.OK + K_2SO_3$. The **$\beta$-naphthol** is prepared in a similar way from the β-naphthalene sulphonic acid.

Usually the **α-naphthol** is contaminated with 5-10 per cent. β-naphthol. It may be prepared pure either by fractionally crystallising its salts, or, better, by decomposing α-naphthylamine with water in an autoclave:—$\alpha.C_{10}H_7.NH_2 + H_2O = \alpha.C_{10}H_7.OH + NH_3$.

Ketones

Anthraquinone, $C_6H_4\langle{CO \atop CO}\rangle C_6H_4$, is manufactured by oxidising anthracene. Finely powdered commercial anthracene (containing 60-90 per cent. anthracene) is agitated with a boiling solution of sodium or potassium bichromate (1 molecule bichromate : 1 molecule of true anthracene), while dilute H_2SO_4 solution (4 molecules H_2SO_4 to every molecule of bichromate used) is slowly run in over nine to ten hours. The mixture is boiled, the crude anthraquinone filtered off, dried, and ground. It is then purified from any phenanthrene, acridine, carbazol, etc., present by heating with two to three times its weight of concentrated H_2SO_4 at 110° C. and pouring the mass into water. The impurities are changed into soluble sulphonic acids, while the anthraquinone is precipitated unchanged. It is washed with soda, filtered, and dried, and then contains 90-95 per cent. pure anthraquinone. It is then used immediately for making alizarin (*q.v.*). Yellow needles, M.P. 277° C. Fuming sulphuric acid converts it into monosulphonic acid, $C_{10}H_7O_2.SO_3H$, which, when fused with caustic soda, yields **alizarin**.

Benzophenone or **Diphenyl Ketone**, $C_6H_5.CO.C_6H_5$, and **Phenylmethylketone** or **Acetophenone**, $C_6H_5.CO.CH_3$, are obtained by the distillation of the calcium salts of the corresponding acids :—

$$\underset{\text{Calcium benzoate.}}{(C_6H_5.CO_2)_2Ca} = \underset{\text{Benzophenone.}}{C_6H_5.CO.C_6H_5} + CaCO_3.$$

$$\underset{\text{Calcium benzoate.}}{(C_6H_5.CO_2)_2Ca} + \underset{\text{Calcium acetate.}}{(C_2H_3O_2)_2Ca} = \underset{\text{Acetophenone.}}{2C_6H_5.CO.CH_3} + 2CaCO_3.$$

Nitro-, amino-, and diamino-derivatives of these bodies are used, *e.g.*, **Diaminobenzophenone**, $NH_2.C_6H_4—CO—C_6H_4.NH_2$, prepared by nitrating benzophenone and then reducing.

Tetramethyldiaminobenzophenone, $CO\langle{C_6H_4.N(CH_3)_2 \atop C_6H_4.N(CH_3)_2}$, is manufactured by passing phosgene gas, $COCl_2$ (prepared by direct union of CO and Cl_2 in sunlight, and, since it easily liquefies at 8° C. under atmospheric pressure, condensed to a liquid by pressure and kept stored up in steel cylinders), is passed into **Dimethylaniline** at ordinary temperatures until the dimethylaniline has increased 50 per cent. by weight :—

$$\underset{\text{Dimethylaniline.}}{2C_6H_5.N(CH_3)_2} + \underset{\text{Phosgene gas.}}{COCl_2} = \underset{\text{Tetramethyldiamino-benzophenone.}}{CO[C_6H_4.N(CH_3)_2]_2} + 2HCl.$$

The liquid is then heated for some time, the excess of dimethylaniline steam-distilled off, the residue dissolved in HCl and precipitated by alkali. Solid; M.P. 179° C. It is converted on a large scale by reducing agents into **Tetramethyldiaminobenzhydrol**, $HO.CH.[C_6H_4N(CH_3)_2]_2$ (see p. 466).

APPENDIX

Preparation of Organic Compounds by Electrical Processes

LITERATURE

WALTHER LÖB'S "Die Elektrochemie der organische Verbindungen." 3rd Edition. Halle, 1905.

ELBS' "Übungsbeispiele für die elektrolytische Darstellung Chemische Präparate." Halle, 1902.

FISCHER'S *Jahresberichte der chem. Technologie.* 1884 onwards.

The electrolytic oxidation and reduction of organic compounds have been the subject of investigation for many years, and has been attended with important technical results.

Thus Elbs and Brunner (*Zeit. f. Elektrochemie*, 6, 604, 1900) obtained a yield of 80 per cent. **formaldehyde** by electrolysing a sulphuric acid solution of **methyl alcohol**.

Iodoform may be prepared by electrolysing a mixture of 14 parts sodium carbonate (anhydrous), 10 parts KI, 100 parts water, 20 parts alcohol, at a temperature of 70° C. :—

$$CH_3.CH_2OH + 10I + H_2O = CHI_3 + CO_2 + 7HI.$$

A quantitative yield of **Bromoform**, $CHBr_3$, is obtained by electrolysing an aqueous solution of acetone and KBr (*Ztschr. für Elektrochemie*, 10, 409, 1904).

Chloral is obtained (*Elektrochem. Ztschr.*, i. 70, 1894) by allowing alcohol to flow into the anode chamber of a cell in which a KCl solution is being electrolysed.

Crude sugar-rich liquids are now purified by electrolytic reduction (*Jahrbuch der Elektrochemie*, 3, 322, 1896; 8, 628, 1901).

Acetone is reduced by electrolysis in an acid or alkali solution to Isopropylalcohol and Pinacone (D. R. Pat., Nr. 113,719, 1899).

Nitrobenzene, $C_6H_5.NO_2$, can be electrolytically reduced in stages, first to azo compounds, then to hydrazo compounds (*Jahresber. d. chem. Tech.* 1894, 1896, 1901). The same holds true of other nitro-aromatic bodies.

Thus, ***m*-Azo-toluol** is obtained by electrolytically reducing nitrotoluols (Rohde, *loc. cit.*, 1899). **Amino** compounds, however, are finally obtained by electrolysing certain nitro-bodies. Thus, ***m*-Nitro-dimethylaniline** gives on electrolytic reduction first **Tetramethyl-*m*-diaminoazobenzol**, and finally **Tetramethyl-*m*-diaminohydrazobenzol**. ***m*-Nitraniline** may be electrolytically reduced to ***m*-Diaminoazobenzol** (Wülfing, 1899).

Farbenfabr. *Bayer* (1901) made the important discovery that **nitro-bodies** are readily reduced to azo and hydrazo compounds without their necessarily being dissolved in a solvent (such as alcohol, nitrobenzene, etc.). The cathode consists of a metal such as zinc, tin, lead, etc., and surrounding it is placed an alkaline solution of the metal and the nitro-body to be reduced. The anode is separated from the cathode by a diaphragm, and consists of carbon, platinum, or some other inactive substance, immersed in a solution of soda, sodium sulphate, or sodium chloride. In the last case chlorine is evolved and may be employed to give rise to chlorine derivatives. The liquid about the cathode is vigorously stirred during the passage of the current. If the nitro-body is volatile, condensers must be attached to the cathodic chambers, since the heat evolved by the current may cause the nitro-body to volatilise. By such an apparatus they convert nitrobenzene completely into azobenzol in six to seven hours, the solid azobenzol separating when the cathodic fluid is cooled and is purified in the usual way. The production of hydrazobenzene requires a longer time.

Paranitrotoluene, $C_6H_4.NO_2.CH_3$, may be completely oxidised to **Paranitrobenzoic Acid**, $C_6H_4.NO_2.COOH$, by dissolving 7.5 parts paranitrotoluene in 40 parts glacial acetic acid, adding 20 parts concentrated H_2SO_4 and 20 parts water and 0.1 part $MnSO_4$, then placing the mixture in the *anodic* compartment of an electrolytic cell, and electrolysing at 80° C. with a current density of 175 amperes per square metre (Boehmiger, *Jahresberichte d. chem. Tech.* 1901).

Aniline may be somewhat similarly oxidised to **Quinone** at the *anode* of an electrolytic cell.

Benzidine may be prepared electrolytically from **nitrobenzene** (see Löb, *Jahresberichte d. chem. Tech.* 1900, 1901). 10 parts of nitrobenzene are dissolved in 50 parts of a 3 per cent. NaOH solution, placed in the cathodic compartment of an electrolytic cell, and vigorously stirred while a current of 10 amperes per 100 sq. cm. is passed at a temperature of 80°-100° C. until the whole is reduced to the azoxy state.

Then 20 parts H_2SO_4 in 50 parts water are added, and reduction carried further at ordinary temperatures, when the azoxybenzene passes completely into benzidine sulphate. *o*-**Nitrotoluene** may be in an exactly similar manner reduced to *o*-azoxytoluene, which is then acidified as above and reduced to tolidine sulphate.

The above brief account gives an idea of the technically important results which can follow the application of electrical processes to organic compounds.

SECTION XIII

Industry of the Synthetic Colouring Matters

INDUSTRY OF THE SYNTHETIC COLOURING MATTERS

By Thomas Beacall, B.A.(Camb.) and G. Martin, Ph.D., M.Sc.

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Read Holliday & Sons.
Cassella & Co.
Farbwerke vorm. Meister Lucius & Brüning.
Badische Anilin- u. Soda-Fabrik.
Kalle & Co.
Levinstein & Co.
Farbenfabrik en vorm. F. Bayer & Co.

Introduction

The origin and development of the coal-tar dye industry represents one of the greatest triumphs of modern chemistry.

In 1834 Runge discovered phenol and aniline in coal-tar. The researches of A. W. Hofmann (1842-63) revealed the chemical nature of several of the more important constituents of coal-tar. The industry practically dates from 1856, when Perkin obtained **Mauve** by oxidising aniline. In 1859 Verguin isolated **Fuchsine**. Soon afterwards **Aniline Blue** was discovered, which Hofmann in 1863 showed to be a derivative of Rosaniline. In 1868 and in 1869 Graebe and Liebermann synthesised **Alizarin** from anthracene by two methods, the second of these being almost simultaneously discovered by Perkin. In 1871 Baeyer discovered the **Phthaleins**. In 1876 E. and O. Fischer worked out the constitution of the **Rosaniline colours**. About the same time the manufacture of the **Azo colours** was begun. In 1884 the **Congo Red Cotton Dyes** were introduced. **Indigo** was synthesised by Baeyer in 1880, but its manufacture only became a commercial success after Heumann's synthesis in 1890, the product being placed on the market by the Badische Anilin- und Soda-Fabrik in 1897. The first sulphur dye, **Cachou de Laval**, was made by Croissant and Bretonnière in 1873, but the sulphide dye manufacture dates practically from **Vidal Black** (1893). In recent years the most noteworthy dates are 1901, the year of the discovery of the first **Anthracene Vat Dyes** by the Badische Anilin- und- Soda Fabrik, and 1905, when **Thioindigo** was produced by Friedländer.

Although the dye industry was founded in England by Perkin, who established a factory for the manufacture of Mauve, and later of Alizarin, the trade has gone largely into German hands. This has been attributed to a variety of causes which cannot be considered at length here. Suffice it to say that probably one of the most weighty of these causes was the unfortunate divorce of science from industry which largely prevailed in this country until recently, whereas the contrary was the case in Germany. It is noteworthy that the men who founded and built up the enormous German

undertakings were not business men in the usual sense of the word, but were themselves chemists of note and realised to the full the importance of research. Then, too, every improvement was patented, and the industry was thus gradually surrounded by a ring of patents, which rendered the entry of new competitors into the market increasingly difficult. Among the German colour factories the following may be especially noted: The Badische Anilin- und Soda-Fabrik in Ludwigshafen am Rhein is the largest chemical factory in the world, employing 7,500 workmen, 197 university trained chemists, 95 engineers, and 709 clerks (1906). The Farbenfabriken vormals F. Bayer & Co. in Elberfeld and Leverkusen is almost as large. Other very large firms are Cassella & Co. in Frankfurt am Main, the Farbwerke vormals Meister Lucius & Brüning of Höchst, the Aktiengesellschaft für Anilin Fabrikation of Berlin, and Kalle & Co. of Biebrich. The most important English firms are Read Holliday & Sons of Huddersfield, and Levinstein & Co. of Manchester.

The worth of the coal-tar colours manufactured annually amounted in 1910 to £20,000,000; over three-quarters of this value are manufactured by the German firms.

Statistics.—The following numbers show the value of the import of synthetic dyes into the United Kingdom (almost entirely from Germany):—

IMPORTS

	1906.	1913.	Value in 1913.
	Cwt.	Cwt.	
Alizarin and anthracene dye-stuffs	57,300	60,800	£272,000
Aniline and naphthalene dye-stuffs	188,600	283,000	1,543,000
Synthetic indigo	39,000	23,900	76,700
Other coal-tar dye-stuffs	700	155	570,000
Total	285,600	367,855	£2,461,700

The export of coal-tar dyes from the United Kingdom amounted in 1910 to 56,000 cwt., value £196,000.

The United States *imported*, principally from Germany:—

	1906.	1910.	Value in 1910.
	Lbs.	Lbs.	
Alizarin colours	3,882,000	3,023,000	$648,000
Coal-tar colours and dyes	...	...	6,911,000
Indigo	7,393,000	7,540,000	1,196,000

The United States exported of dyes and dye-stuffs—$491,000 in 1906, and $380,000 in 1910.

The German net export of coal-tar colours (including aniline oils and intermediate products) amounted in 1909 to 1,600,000 cwt. (more exactly, 83,250 metric tons), having a net value of £10,000,000.

For statistics regarding **Indigo** see p. 461.

Almost all the artificial colouring matters are derivatives of benzene, naphthalene, or anthracene, which are obtained from coal-tar. 1,000 tons of coal-tar yield, when worked up, 2.5 tons of fuchsine, 0.75 ton of indigo, 0.2 ton of alizarin, and 0.2 ton of picric acid. Since the number of artificial dye-stuffs runs into several thousands, it is impossible within the limits of the present article to mention more than a few of the more important of each separate group, placing special emphasis on new classes of dye-stuffs, such as have been specially developed within the last few years. For particulars of special dyes the reader must consult the works cited at the beginning of this section.

Classification of Dyes.—Dyes may be classified either according to their chemical composition or according to their dyeing properties. In discussing the manufacture of dyes, the former method of procedure is the only suitable one, the second method being used when the technology of dyeing is under consideration.

The following scheme shows the arrangement followed in the present article, the three groups which are of the greatest importance at the present time being considered first:—

1. Azo dyes (including pyrazolone and stilbene dyes).
2. Dyes of the anthracene series.
3. Dyes of the indigo and thioindigo series.
4. Di- and tri-arylmethane dyes.
5. Pyrone dyes.
6. Azine dyes.
7. Oxazine dyes.
8. Dyes containing sulphur (thiazine, thiazole, and sulphide dyes).
9. Acridine dyes.
10. Minor groups of dyes—nitro and nitroso dyes, quinoline dyes, oxyketone dyes, indophenols, indamines, aniline black.

We will take them in this order in the following pages.

1. AZO DYES

The azo dyes form the largest group of dyes known; they derive the name from their characteristic **azo** group, consisting of two nitrogen atoms and usually written —N=N—, or —N_2—. According as the azo group occurs one, two, three, four, etc., times in the molecule, the dyes are described as monoazo, disazo, trisazo, tetrakisazo, etc.

The azo dyes were discovered by Griess in 1858 and some were put on the market soon afterwards, but as a class the dyes did not come into existence until about 1876.

Method of Preparation.—When a primary amine is treated with nitrous acid at a low temperature, diazo compounds are formed according to the equation:—

$$\underset{\text{Amine.}}{R.NH_2} + \underset{\text{Nitrous acid.}}{HNO_2} = \underset{\text{Diazo hydroxide.}}{R.N{=}N.OH} + H_2O.$$

In practice aromatic amines only are used, and nitrous acid is replaced by sodium nitrite and an acid, usually hydrochloric acid. The reaction then becomes:—

$$\underset{\text{Amine.}}{R.NH_2} + NaNO_2 + 2HCl = \underset{\text{Diazo chloride.}}{R.N{=}N.Cl} + NaCl + 2H_2O.$$

The diazo compounds can then react with other compounds, usually aromatic amines or phenols, producing azo compounds, which, if of suitable constitution, act as dyes. The reaction is:—

$$\underset{\text{Diazo compound.}}{R.N{=}N.Cl} + \underset{\text{Second component.}}{R^1H} = \underset{\text{Azo compound.}}{R.N{=}N.R^1} + HCl.$$

The amine which is diazotised is referred to as the diazo or first component, while the compound R^1H is called the second component.

The operation is carried out in practice as follows:—

A molecular proportion of the amine to be diazotised is dissolved in water with about 2½ molecular parts of hydrochloric acid; a solution of a molecular part of nitrite is then run in gradually while the reaction mixture is kept cool and stirred. After diazotisation is complete, the solution is added to a solution of a molecular proportion of the second component, and stirring is continued until the combination is finished; the dye either precipitates or is salted out by means of salt or hydrochloric acid, and is filtered off, washed and dried.

The diazo reaction is capable of very wide application, but some amines cannot be diazotised except under special conditions, while others do not give the normal diazo salts—some of these will be noted later. The diazo compounds in general are not very stable, accordingly some amines (aniline, toluidines, etc.) must be

diazotised at 0° C., while for others (nitranilines, naphthylamines, etc.) a temperature of about 10° C. is suitable. In some cases (*e.g.*, trinitraniline) the diazotisation is effected by nitrite in the presence of cold concentrated sulphuric acid, while the 1 : 2- and 2 : 1-aminonaphthols are diazotised in the presence of salts of copper, zinc, etc.

Besides nitrite, various other diazotising agents are occasionally employed, for instance, nitrosyl chloride, and nitrosulphonic acid.

It is unnecessary here to consider further the nature of the diazo compounds, or the various formulæ which have been proposed for them. A full discussion of these will be found in Cain's "Chemistry of the Diazo Compounds" (Arnold, 1908). Kekulé's formula, R.N=N.X, expresses the facts sufficiently for our present purpose.

In connection with the operation of coupling the diazo compounds with the second component, the following points should be noted: phenols are coupled in an alkaline solution (sodium carbonate), while if the second component is an amine it is coupled in a neutral or acid (usually hydrochloric or acetic) solution.

The azo group generally enters the molecule of the second component in the para-position to the amino or hydroxyl group of this body, or, if this combination be impossible, in the ortho-position. Thus aniline, phenol, α-naphthol, α-naphthylamine couple in the para-position, *p*-toluidine and *p*-cresol in the ortho-position, while β-naphthol couples in the α-ortho-position. In the case of the naphthylamine or naphthol sulphonic acids, the positions of the sulphonic groups often determine the position taken up by the azo group. In the case of some of the heteronticlear aminonaphthol sulphonic acids, *e.g.*, the 2 : 8 : 6, 2 : 5 : 7, 1 : 8 : 4, 1 : 8 : 5, 1 : 8 : 3 : 6 acids, different products are obtained according as the combination is effected in alkaline or in acid solution—in alkaline solution the azo group enters in ortho-position to the hydroxyl group, while in hydrochloric acid solution it enters in ortho-position to the amino group.

An important variation in the process of preparing azo dyes is the production of these dyes "**on the fibre**." A typical instance is **Paranitraniline red**; to produce this dye, the material to be dyed is impregnated with β-naphthol by passage through an alkaline bath of this compound, and is then passed into a second bath containing diazotised *p*-nitraniline, the dye thus being produced on the material. For use in this process the diazotised *p*-nitraniline is sometimes converted by the action of caustic alkali into a stable isomeric form, the so-called nitrosamine, which may be formulated $NO_2.C_6H_4.NNa.NO$, and is sold as such; when required for use, the nitrosamine is reconverted into the active diazo compound by treatment with acid (see pp. 450, 478, 545, 558).

Monoazo Dyes, R.N=N.R¹

The monoazo dyes are prepared according to the methods described above; their number is very great, and only a few typical ones are described here. Their dyeing properties vary according to their constitution; a large number dye wool in acid baths; an important and growing group of these consists of the so-called ortho-oxyazo dyes, obtained from diazotised *o*-aminophenolic compounds—these dye wool with chrome mordants; a large number of monoazo dyes are used as parent materials for the manufacture of pigments or lakes. Some typical monoazo dyes are tabulated below:—

Acid Wool Dyes

Acid yellow	Aminoazobenzene disulphonic acid.
Azococcine 2R	Xylidine + 1 : 4-naphthol sulphonic acid.
Crystal Ponceau ,, scarlet 6R	α-Naphthylamine + 2 : 6 : 8-naphthol disulphonic acid.
Fast red A	Naphthionic acid + β-naphthol.
,, ,, B	α-Naphthylamine + 2 : 3 : 6-naphthol disulphonic acid.
Lanacyl blue BB	1 : 8 : 3 : 6-aminonaphthol disulphonic acid + 1 : 5-aminonaphthol.
Metanil yellow	Metanilic acid + diphenylamine.
Orange II	Sulphanilic acid + β-naphthol.
Palatine red	α-Naphthylamine + 1 : 3 : 6-naphthol disulphonic acid.
Ponceau 2G	Aniline + 2 : 3 : 6-naphthol disulphonic acid.
,, 2R	*m*-Xylidine + 2 : 3 : 6-naphthol disulphonic acid.
,, 4R	ψ-Cumidine + 2 : 3 : 6-naphthol disulphonic acid.
,, 6R	Naphthionic acid + β-naphthol trisulphonic acid.
Tropaeoline O	Sulphanilic acid + resorcin.

Dyes for Chrome-Mordanted Wool

(*a*) **From Diazotised *o*-Aminophenols.**—Most of these dyes are of recent introduction, so it is difficult to ascertain the trade name of a dye of a particular constitution. Typical combinations are:—

4-acetylamino-2-aminophenol-5-sulphonic acid + β-naphthol, etc. (Cassella, English Patent, 3,182, 1903).

1-amino-2-naphthol sulphonic acids + naphthols, naphthol sulphonic acids, aminonaphthols, aminonaphthol sulphonic acids, dioxynaphthalenes, dioxynaphthalene sulphonic acids, resorcin, *m*-aminophenol, *m*-diamines, etc. (Geigy, English Patent, 15,025, 1904).

o-aminophenol and its methyl, chlor, nitro, etc., derivatives + chromotropic acid (M.L.B., English Patent, 26,383, 1905).

Nitro or chlor derivatives of *o*-aminophenol + 2-arylamino-5-naphthol-7-sulphonic acids (Bayer, English Patent, 14,921, 1906).

Nitro or chlor derivatives of *o*-aminophenol + alkyl or aryl derivatives of *m*-aminophenol (Bayer, English Patent, 25,177, 1908).

(*b*) **Other Dyes for Chrome-Mordanted Wool.**—

Alizarine yellow GG	*m*-Nitraniline + salicylic acid.
Azochromine	*p*-Aminophenol + pyrogallol.
Azofuchsine B	Toluidine + 1 : 8 : 4-dioxynaphthalene sulphonic acid.
Chromotrope 2B	*p*-Nitraniline + 1 : 8 : 3 : 6-dioxynaphthalene disulphonic acid.
Diamond yellow R	Anthranilic acid + salicylic acid.
Milling yellow	2-Naphthylamine sulphonic acid + salicylic acid.

Dyes used in the Manufacture of Lakes

Many of these dyes also are of recent introduction, so the trade names are difficult to obtain.

One of the best known is Lithol red (2-naphthylamine-1-sulphonic acid + β-naphthol) (B.A.S.F., English Patent, 25,511, 1899).

Other typical combinations are:—

o-Nitraniline-*p*-sulphonic acid or *p*-nitraniline-*o*-sulphonic acid + β-naphthol (M.L.B., English Patent, 16,409, 1901).

Aniline, etc. + 2 : 3-oxynaphthoic acid (Akt. Ges. für Anilin Fabrikation, English Patent, 1,235, 1903).

2-Naphthylamine disulphonic acids + naphthol sulphonic acids (Bayer, English Patent, 12,512, 1904).

Nitrochloranilines + β-naphthol (B.A.S.F., English Patents, 6,227, 1907, and 6,228, 1907).

Direct Cotton Dyes

The combination of diazotised dehydrothiotoluidine sulphonic acid or primuline (see p. 478) with various components give cotton dyes, *e.g.*—

Oriol yellow—primuline + salicylic acid.

Rosophenine 10B—dehydrothiotoluidine sulphonic acid + 1-naphthol-4-sulphonic acid.

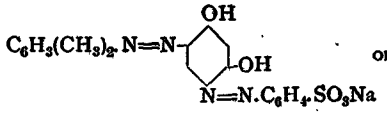
Various derivatives of 2 : 5 : 7-aminonaphthol sulphonic acid when combined with diazo compounds (aniline, toluidine, xylidine, naphthylamines, etc.) give cotton dyes, *e.g.*—

2-acetylamino-5-naphthol-7-sulphonic acid, 2-benzoylamino-5-naphthol-7-sulphonic acid, aminobenzoyl-2-amino-5-naphthol-7-sulphonic acids, aminophenyl-1 : 2-naphthothiazole-5-oxy-7-sulphonic acids, aminophenyl-1-2-naphthiminazole-5-oxy-7-sulphonic acids, etc.

Disazo Dyes, $R.N{=}N.R'.N{=}N.R''$

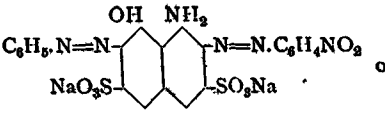
There are three main types of disazo dyes: (*a*) primary, (*b*) secondary, (*c*) disazo dyes from tetrazotised diamines.

(*a*) **Primary Disazo Dyes.**—Certain azo dye components can be coupled with two diazo groups; such components are phenol, resorcin, α-naphthol, *m*-phenylenediamine, *m*-toluylendiamine, *m*-aminophenol, the aminonaphthol sulphonic acids referred to above, which can be coupled in acid or alkaline solution yielding different products, and the 1 : 8-dioxynaphthalene-4-sulphonic acid or -3 : 6-disulphonic acid. To prepare the primary disazo dyes, two molecular proportions of an amine, or one molecular proportion of each of two different amines, are diazotised and coupled with one molecular proportion of the second component. Thus **Resorcin Brown** is obtained by coupling *m*-xylidine (1 molecule) and sulphanilic acid (1 molecule) with resorcin (1 molecule).



or, *m*-Xylidine + Sulphanilic acid → Resorcin.

Naphthol Blue-Black is obtained by coupling 1 : 8-aminonaphthol 3 : 6-disulphonic acid (H acid) first with *p*-nitraniline in acid solution, and then with aniline in alkaline solution.



or, *p*-Nitraniline + Aniline → H-acid.

It dyes wool in an alkaline bath.

Other primary disazo dyes are—

Terracotta F (dyes cotton).—Sodium salt of—

*Primuline + Naphthionic acid → *m*-phenylenediamine.

Cotton Orange R (dyes cotton)—

Primuline + Metanilic acid → *m*-phenylenediaminedisulphonic acid.

Fast Brown (acid wool dye)—

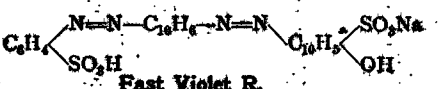
Naphthionic acid + Naphthionic acid → resorcin.

(*b*) **Secondary Disazo Dyes** are obtained by coupling diazotised aminoazo compounds with amines, phenols, etc. In order, therefore, to prepare bodies of this type it is necessary to diazotise *twice*—first an amine is diazotised, then the diazo salt thus produced is coupled directly to another amine—the "middle" component—and the amino group in the aminoazo body thus produced is then diazotised, and finally the product thus obtained is coupled with an amine, phenol, etc.

The amines employed as "middle components" must be of such a nature that when combined with the first component they can be rediazotised to yield a diazo salt. Thus the amines generally employed are those which, on coupling with the first component, give either para-aminoazo compounds, or aminoazo compounds containing the amino and azo groups in different nuclei; examples of the first type are aniline, *o*- and *m*-toluidine, *p*-xylidine, *o*-anisidine, cresidine, α-naphthylamine and its 6- and 7-sulphonic acids (**Cleve's acids**); examples of the second type are 2 : 5 : 7- and 2 : 8 : 6-aminonaphthol sulphonic acids, combined in alkaline solution, and the recently discovered derivatives of aminonaphthol sulphonic acids containing a heteronuclear amino group, such as the aminophenyl-1 : 2-naphthiminazoleoxy-sulphonic acids, and the aminobenzoylaminonaphthol sulphonic acids.

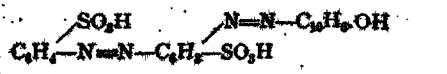
* See p. 478.

An example of such dyes is **Fast Violet R**, produced by (1) diazotising sulphanilic acid; (2) coupling the diazo compound with α-naphthylamine, giving $C_6H_4\begin{matrix}N{=}N{-}C_{10}H_6{\cdot}NH_2\\SO_3H\end{matrix}$; (3) diazotising once again; and (4) coupling with β-naphthol sulphonic acid S, thus obtaining the dye—



Fast Violet R.

Biebrich Scarlet is prepared by coupling aminoazobenzene disulphonic acid with β-naphthol, and has, therefore, the constitution—



Other secondary disazo dyes are—

Brilliant Croceine M (acid wool dye).—Aminoazobenzene + 2 : 6 : 8-naphtholdisulphonic acid.

Cloth Scarlet G (acid wool dye).—Aminoazobenzenesulphonic acid + β-naphthol.

Croceine Scarlet 7B } (acid wool dye).—Aminoazotoluene sulphonic acid + 2 : 8-naphtholsulphonic
" " **8B** } acid.

Diaminogen (dyes unmordanted cotton blue).—Acetyl-1 : 4-naphthylenediamine-6- and -7-sulphonic acid + α-naphthylamine + 2 : 6-naphthol sulphonic acid (product saponified).

Janus Red (dyes cotton and wool).—*m*-Aminophenyltrimethylammonium chloride + *m*-toluidine + β-naphthol.

Naphthylamine Black D (acid wool dye).—Naphthylamine disulphonic acid + α-naphthylamine + α-naphthylamine.

Ponceau 4RB } (dyes wool and cotton).—Aminoazobenzene sulphonic acid + 2 : 8-naphthol
Croceine Scarlet 3B } sulphonic acid.

Recently a number of secondary disazo dyes have been prepared having 2 : 5 : 7-aminonaphthol sulphonic acid and its alkyl, aryl, acidyl, etc., derivatives as end components. These dye cotton blue to violet shades. (See English Patents, Nos. 14,248, 1907; 4,767, 1909; 4,768, 1909; 11,364, 1909.)

(*c*) **Disazo Dyes from Tetrazotised Diamines.**—This type of disazo dyes is prepared by tetrazotising, *i.e.*, diazotising both the amino groups of a primary diamine and combining the tetrazo compound so obtained either with two molecular proportions of one dye component or with one molecular proportion of one component and one molecular proportion of another component; in the first case the dyes are referred to as "symmetrical" and in the second case as "mixed" disazo dyes.

The most important diamines in this connection are the so-called para-diamines, of which benzidine, $H_2N{-}C_6H_4{-}C_6H_4{-}NH_2$, is typical; other well-known diamines of the benzidine type are *o*-tolidine, dianisidine, diethoxybenzidine, benzidine-*o*-disulphonic acid, benzidine sulphone. Similar diamines containing two benzene nuclei connected by another group and containing in each nucleus an amino group, usually in the para-position to the connecting group, are diaminostilbene disulphonic acid, *p*-diaminodiphenylurea, azoxyaniline, etc. The dyes derived from these diamines possess in general the highly important property of dyeing cotton directly (*i.e.*, without mordants), and hence are known as **direct or substantive cotton dyes.**

It should be noted, however, that the dyes derived from *m*-tolidine, *m*-dichlorbenzidine and benzidine-*m*-disulphonic acid do not dye cotton, but are acid wool dyes. It should be noted further that all diamines cannot be tetrazotised—thus ortho- and peri-diamines do not yield tetrazo salts but ring compounds, azimides. Some meta-diamines, *e.g.*, *m*-phenylenediamine, can be tetrazotised

like the paradiamines. The case of *p*-phenylenediamine requires special mention; this body cannot be readily tetrazotised; accordingly disazo dyes are prepared from this body by first diazotising *p*-nitraniline or an acidyl- (*e.g.*, acetyl) -*p*-phenylenediamine, combining the diazo compound with a dye component, reducing the nitro group or saponifying the acidylamino group, of the dye so obtained, then diazotising the amino group so produced and combining with a second molecule of a dye component. A similar process is employed with the sulphonic acids of 1 : 4-naphthylenediamine.

The following are typical dyes of this class; except where otherwise stated, they dye unmordanted cotton:—

a. Derived from Benzidine and its Derivatives

Benzopurpurine B	Tolidine	2-naphthylamine-6-sulphonic acid. 2-naphthylamine-6-sulphonic acid.
„ 4B	Tolidine	naphthionic acid. naphthionic acid.
„ 6B	Tolidine	1-naphthylamine-5-sulphonic acid. 1-naphthylamine-5-sulphonic acid.
„ 10B	Dianisidine	naphthionic acid. naphthionic acid.
Congo Blue 2B	Dianisidine	1-naphthol-4-sulphonic acid. 2-naphthol-3 : 6-disulphonic acid.
Congo Corinth G	Benzidine	naphthionic acid. 1-naphthol-4-sulphonic acid.
„ B	Tolidine	1-naphthol-4-sulphonic acid. 1-naphthol-4-sulphonic acid.
Congo Red	Benzidine	naphthionic acid. naphthionic acid.
„ 4R	Tolidine	naphthionic acid. resorcin.
Diamine Black BH	Benzidine	2 : 8 : 6-aminonaphthol sulphonic acid (alkaline coupling). 1 : 8 : 3 : 6-aminonaphthol sulphonic acid (alkaline coupling).
Diamine Blue BB	Benzidine	1 : 8 : 3 : 6-aminonaphthol sulphonic acid (alkaline coupling). 1 : 8 : 3 : 6-aminonaphthol sulphonic acid (alkaline coupling).
Diamine Brown B	Benzidine	salicylic acid. 2-phenylamino-8-naphthol-6-sulphonic acid (alkaline coupling).
Diamine Red 3B **Deltapurpurine 7B**	Tolidine	2-naphthylamine-7-sulphonic acid. 2-naphthylamine-7-sulphonic acid.
Dianol Brilliant Red **Tolulylene Red**	Dichlorbenzidine	2 : 3 : 6-naphthylamine disulphonic acid. 2 : 3 : 6-naphthylamine disulphonic acid.
Oxamine Red	Benzidine	salicylic acid. 2 : 5 : 7-aminonaphthol sulphonic acid (alkaline coupling).

b. DERIVED FROM PHENYLENE AND NAPHTHYLENE DIAMINES

Azoalizarine Bordeaux W (dyes wool with chrome mordants)—

p-phenylenediamine → Salicylic acid. + 1·4-naphthol sulphonic acid.

Bismarck Brown, Manchester Brown (dyes wool, leather, and tannin mordanted cotton)—

m-phenylenediamine → *m*-phenylenediamine. + *m*-phenylenediamine.

Coomassie Black B (dyes wool)—

1 : 4-diaminonaphthalene-2-sulphonic acid → 2 : 3 : 6-naphthol disulphonic acid. + 2-naphthylamine.

Naphthylene Red—

1 : 5-diaminonaphthalene → naphthionic acid. + naphthionic acid.

Toluylene Orange RR—

Toluylenediamine sulphonic acid → 2-naphthylamine. + 2-naphthylamine.

c. DERIVED FROM OTHER DIAMINES

Benzo Fast Pink 2BL—

p-diaminodiphenylurea disulphonic acid → 2 : 8 : 6-aminonaphthol sulphonic acid. + 2 : 8 : 6-aminonaphthol sulphonic acid.

Brilliant Yellow—

diaminostilbene disulphonic acid → phenol. + phenol.

Diphenyl Fast Black—

p-diaminoditolylamine → 2 : 8 : 6-aminonaphthol sulphonic acid (alkaline coupling). + *m*-toluylene diamine.

Hessian Yellow—

Diaminostilbene disulphonic acid → salicylic acid. + salicylic acid.

St Denis Red—

Diaminoazoxytoluene → 1 : 4-naphthol sulphonic acid. + 1 : 4-naphthol sulphonic acid.

Trisazo Dyes, $R.N{=}N.R'.N{=}N.R''.N{=}N.R'''$

Dyes containing three azo groups can be produced in a variety of ways :—

1. From Secondary Disazo Dyes—

(*a*) Where the end component of a secondary disazo dye is an amine capable of diazotisation, it may be diazotised and coupled with another component.

$$R.N{=}N.R'.N{=}N.R''.NH_2 \rightarrow R.N{=}N.R'.N{=}N.R''.N{=}N.Cl \rightarrow R.N{=}N.R'.N{=}N.R''.N{=}N.R'''$$

EXAMPLE.—Acetyl-1 : 4-naphthylenediamine-7-sulphonic acid → Clève's acid → Clève's acid → 2 : 5 : 7-aminonaphthol sulphonic acid. (For Clève's acids, see p. 444.)

A similar dye is—

Clève's acid → Clève's acid → Clève's acid → 2 : 5 : 7-aminonaphthol sulphonic acid.

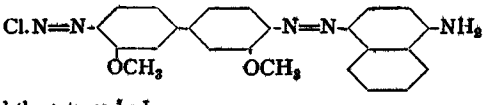
(*b*) When the end component of a secondary disazo dye is a component capable of combining with two azo groups, it may be combined with a further diazo compound. Similar products result on combining such a "double coupling" component with one molecular proportion of a diazoazo compound and one molecular proportion of a diazo compound.

EXAMPLE.—Chrome Patent Green A—
p-aminosalicylic acid—→α-naphthylamine—→1 : 8 : 4 : 6-aminonaphthol sulphonic acid←—aniline.

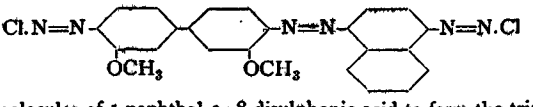
2. From Tetrazotised Diamines—

(*a*) By combining a tetrazotised diamine, such as benzidine, etc., with 1 molecule of a diazotisable middle component, *e.g.*, α-naphthylamine, an intermediate compound is formed, which is then diazotised, thus giving a tetrazo body which is combined with two molecules of a component or one molecule of each of two components.

EXAMPLE.—Thus: dianisidine is tetrazotised and combined with 1 molecule of α-naphthylamine, giving the intermediate compound—

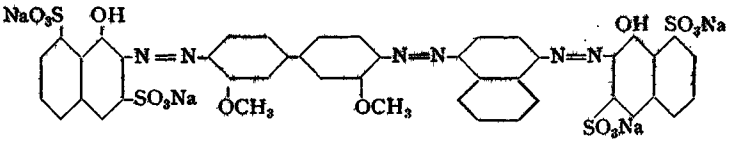


which is diazotised, and the tetrazo body—



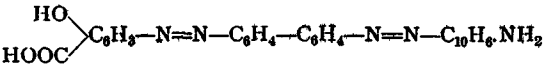
is combined with 2 molecules of 1-naphthol-3 : 8-disulphonic acid to form the trisazo dye—

Congo Fast Blue B—

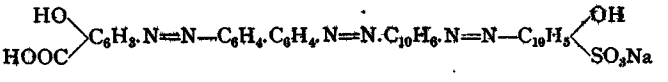


(*b*) If a tetrazotised diamine is combined with a molecule of a diazotisable amine and 1 molecule of another component to form a "mixed" disazo dye, the amino group of the middle component can then be diazotised and combined with an end component.

EXAMPLE.—Benzidine is combined with 1 molecule α-naphthylamine and 1 molecule salicylic acid, giving—



The amino group is then diazotised and the diazo compound coupled with 1-naphthol-4-sulphonic acid, giving **Benzo Grey**—



The following are typical dyes produced by the methods *2a* and *2b* (above):—

Crumpsall Direct Fast Brown O — Benzidine — salicylic acid. / aniline—→2-phenylamino-8-naphthol-6-sulphonic acid.

Diamine Beta Black — Benzidine — 1 : 8 : 3 : 6-aminonaphtholdisulphonic acid. / *p*-xylidine—→1 : 8 : 3 : 6-aminonaphtholdisulphonic acid.

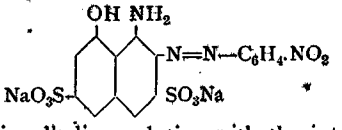
Diamine Bronze G — Benzidine — salicylic acid. / 1 : 8 : 3 : 6-aminonaphtholsulphonic acid—→*m*-phenylenediamine.

Oxamine Violet RR — Benzidine — 1 : 4-naphthol sulphonic acid. / *m*-phenylenediamine oxamic acid→1 : 4-naphthol sulphonic acid.

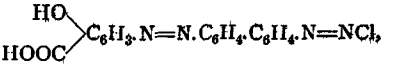
In each of the above processes, *2a* and *2b*, when *p*-phenylenediamine is employed, a procedure is adopted similar to that described under disazo dyes, *p*-nitraniline or acidyl-*p*-phenylenediamine being the starting point, and the nitro

group being reduced, or the acidylamino group saponified at a suitable stage of the process. The process is similar in the case of 1 : 4-naphthylenediamine sulphonic acids.

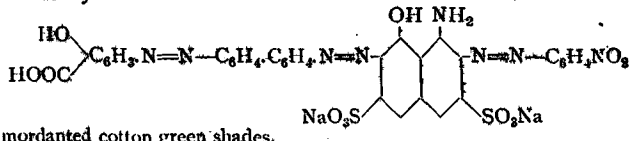
3. A further method may be illustrated by the dye **Diamine Green G**; *p*-nitraniline is diazotised and combined in acid solution with 1 : 8-aminonaphthol-3 : 6-disulphonic acid, giving the monazo dye—



This is then combined in alkaline solution with the intermediate compound from 1 molecule of tetrazotised benzidine and 1 molecule of salicylic acid—



giving the trisazo dye—



This dyes unmordanted cotton green shades.

Other dyes of this type are **Columbia Green, Diamine Green B, Diphenyl Green G** and **3G, Diamine Black HW, Diamine Black R.** All these are direct cotton dyes.

A similar method consists in taking a primary disazo dye in which, say, *p*-nitraniline or acet-*p*-phenylenediamine is one of the diazo components, reducing or saponifying, diazotising the free amino group so produced and combining with a component. Thus, a 1 : 8-aminonaphthol, -dioxynaphthylene, or -naphthylene-diamine sulphonic acid is combined with 1 molecule diazo compound and 1 molecule *p*-nitraniline or acetyl-*p*-phenylenediamine, the product reduced or saponified, diazotised, and combined with amines or phenols.

Another type is afforded by 1 : 8 : 4-aminonaphthol sulphonic acid which can combine with 3 molecules of a diazo compound.

Finally, we may note a case in which a triamine is diazotised and combined with 3 molecules of a component—

Alizarine Yellow FS . . . . . *Magenta ← Salicylic acid. / Salicylic acid. / Salicylic acid.

Tetrakisazo Dyes, R.N=N.R'.N=N.R".N=N.R'".N=N.R''''

Here again various methods may be used A few examples are:—

Benzo Brown G—

Sulphanilic acid
m-phenylenediamine → *m*-phenylenediamine.
m-phenylenediamine → *m*-phenylenediamine.
Sulphanilic acid

Mekong Yellow G—

Benzidine → Salicylic acid.
Benzidine → Dioxydiphenylmethane.
Benzidine → Salicylic acid.

Cuba Black, Diamond Black—

Benzidine → 2 : 8 : 6-Aminonaphtholsulphonic acid → *m*-phenylenediamine.
Benzidine → 2 : 8 : 6-aminonaphtholsulphonic acid → *m*-phenylenediamine.

* See p. 469.

Higher polyazo dyes are known, but need not be discussed here, as they are not made or used to any great extent.

Developing Dyes

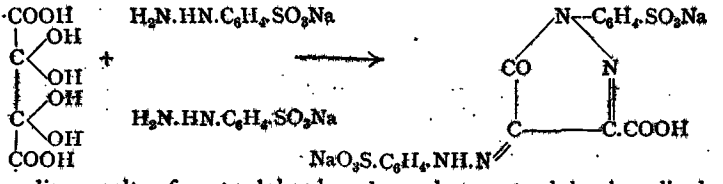
Many azo dyes are capable of conversion into azo dyes of a higher order by "development" on the fibre; the process is analogous to the production of **paranitraniline red** previously referred to (see pp. 442, 478, 545, 558).

Two cases arise: (*a*) when the end component of an azo dye is a diazotisable amine, the dye is applied to cotton and is then diazotised in a bath of nitrite and acid, and then passed through a bath containing β-naphthol or other component; (*b*) when the end component is a compound capable of combining with two azo groups, the dyed material is passed through a bath containing a diazo compound, *e.g.*, diazotised *p*-nitraniline.

Pyrazolone Dyes

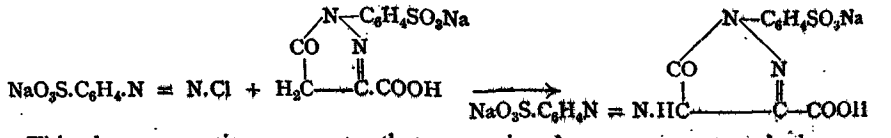
It will be convenient here to consider a group of dyes the constitution of which does not seem to be definitely established; from their method of preparation they may be regarded as containing either azo or hydrazone groups.

The prototype of these dyes is **Tartrazine**, a valuable yellow acid wool dye. Tartrazine was first prepared by condensing 1 molecule of dioxytartaric acid with 2 molecules of phenylhydrazine-*p*-sulphonic acid: thus—



i.e., the sodium salt of 1-*p*-sulphophenyl-3-carboxy-4-*p*-sulphophenylhydrazone-5-pyrazolone.

Tartrazine is also produced by condensing phenylhydrazine-*p*-sulphonic acid (1 molecule) with oxalacetic ester (1 molecule), which yields the ester of 1-*p*-sulphophenyl-3-carboxy-5-pyrazolone, saponifying this ester, and acting upon it with diazotised sulphanilic acid (1 molecule)—



This latter reaction suggests that tartrazine is an azo, not a hydrazone, compound.

A large number of similar dyes have been prepared recently by combining various diazo compounds with pyrazolones, such as the 1-*p*-sulphophenyl-3-carboxy-5-pyrazolone formulated above, the 1-*p*-sulphophenyl-3-methyl-5-pyrazolone, and the two corresponding pyrazolones containing no sulphonic group. Generally these dyes give bright yellow, orange, or red shades; many are suitable for dyeing wool, others serve as the starting point for lakes, while some which contain a residue of benzidine, etc., dye unmordanted cotton.

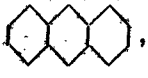
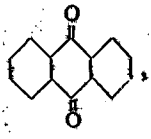
Stilbene Dyes (see p. 544)

Dyes containing a stilbene residue and obtained by tetrazotising diaminostilbene disulphonic acid and coupling with components, have already been considered. There remains a group of dyes also containing the stilbene residue and probably containing azo groups, although they are not formed by the reactions of diazotising and coupling. On heating *p*-nitrotoluene sulphonic acid with aqueous caustic alkalis a complicated reaction (or series of reactions) occurs, the chief products of which are yellow dyes, known as **Curcumine S** or **Sun Yellow, Direct Yellow, Mikado Orange, Stilbene Yellow**, etc., which dye unmordanted cotton.

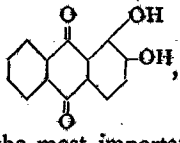
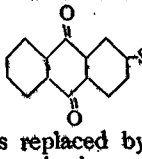
Curcumine S was formerly considered to be azoxystilbene disulphonic acid, and **Direct Yellow** dinitrosostilbene disulphonic acid, but according to Green and Crosland (*Journ. Chem. Soc.*, 89, 1602), these dyes are more complex and contain two stilbene groups, Stilbene Yellow 4G and 8G being dinitroazodistilbenedisulphonic acid, Direct Yellow being mainly azoazoxydistilbenedisulphonic acid, and Mikado Orange chiefly disazodistilbenedisulphonic acid.

A number of other dyes of this class have been prepared, but little is known of their constitution; **Polychromine B** and **Diphenyl Orange RR** are obtained by heating *p*-nitrotoluene sulphonic acid and *p*-phenylenediamine with caustic soda; **Curcuphenine** is similarly obtained from *p*-nitrotoluene sulphonic acid and dehydrothiotoluidine sulphonic acid.

2. DYES DERIVED FROM ANTHRACENE

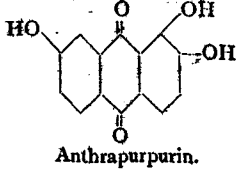
Under this heading are grouped a large number of dyes of varied structure and properties but possessing the common feature that the starting point in the preparation of each is anthracene, $C_{14}H_{10}$,  , a residue or residues of this body or its oxidation product anthraquinone, $C_{14}H_8O_2$,  , being always present in the molecule of these dyes.

The first group of these dyes to be considered is the oxyanthraquinones of which alizarin is the prototype.

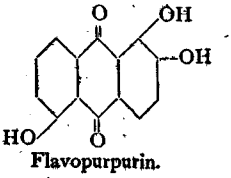
Alizarin or 1 : 2-dioxyanthraquinone,  , is one of the oldest dyes in use and, after indigo, is perhaps the most important. It occurs in nature in madder in the form of a glucoside and was first obtained from this source. The natural alizarin is now almost entirely superseded by the synthetic product. Alizarin was first synthesised in 1868 by Graebe and Liebermann. In 1869 another and better synthesis was effected by them, and almost simultaneously by Perkin. This process consisted in sulphonating anthraquinone to produce the *β*-sulphonic acid,  . By fusing this body with caustic alkali the sulphonic group is replaced by a hydroxyl group and at the same time another hydroxyl group enters in the *α*-position. This process has since been improved by the addition of oxidising agents, such as $KClO_3$, to the alkali, and this is now the usual process for preparing this dye. Alizarin is a mordant dye giving different shades with various mordants. Its chief application is for dyeing bright yellowish red shades on cotton mordanted by Turkey red oil (see p. 43) and alumina.

Closely related to alizarin are two trioxyanthraquinones :—

Anthrapurpurin, 1 : 2 : 7-trioxyanthraquinone, and **Flavopurpurin**, 1 : 2 : 6-trioxyanthraquinone :—



Anthrapurpurin.



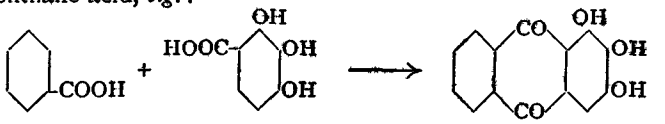
Flavopurpurin.

These bodies are obtained by fusing with caustic alkalis the disulphonic acids which are obtained by sulphonation of anthraquinone.

Commercial alizarin often contains one or both of these bodies, since the anthraquinone sulphonic acid used for the manufacture of alizarin often contains a certain amount of the disulphonic acids. Both these trioxyanthraquinones dye alumina-mordanted cotton red shades.

A third trioxyanthraquinone, **Purpurin**, 1 : 2 : 4-trioxyanthraquinone, which occurs with alizarin in madder, is obtained by oxidising alizarine by manganese dioxide and sulphuric acid, and also dyes red shades with alumina mordants.

A fourth trioxyanthraquinone, **Anthragallol**, 1 : 2 : 3-trioxyanthraquinone, is obtained by an entirely different process, viz., condensation of gallic acid with benzoic or phthalic acid, *e.g.* :—



It dyes brown with chrome mordants.

Alizarin Bordeaux, 1 : 2 : 5 : 8-tetraoxyanthraquinone, is obtained by treating alizarin with fuming sulphuric acid, whereby a sulphuric ester of the tetraoxy body is first formed, and is then saponified; it dyes wool bordeaux with alumina mordants, and violet-blue with chrome mordants.

Alizarin Cyanine R, 1 : 2 : 4 : 5 : 8-pentaoxyanthraquinone, is formed by oxidising **Alizarin Bordeaux** by various oxidising agents, *e.g.*, manganese dioxide in sulphuric acid, arsenic acid, lead peroxide, persulphates, nitric acid, or by electrolytic oxidation; it dyes blue to violet shades with mordants.

Similar oxidation of this pentaoxy body gives a hexaoxyanthraquinone :—

Anthracene Blue, 1 : 2 : 4 : 5 : 6 : 8-hexaoxyanthraquinone, is obtained by treating with sulphuric acid and sulphur sesquioxide, 1 : 5 or 1 : 8-dinitroanthraquinone, or the mixture of these two bodies formed by nitrating anthraquinone; apparently the nitro groups are reduced to amino groups, which are then replaced by hydroxyl groups, while the other hydroxyl groups enter the molecule; the dyeing properties of this dye are similar to those of Alizarin Cyanine R.

Rufigallol, 1 : 2 : 3 : 5 : 6 : 7-hexoxyanthraquinone, is obtained by condensation of 2 molecules of gallic acid (*cf.* **Anthragallol** above); it dyes brown with chrome mordants.

It will be noticed that all the above-described oxyanthraquinones are mordant dyes, and all contain at least two hydroxy groups in ortho-position to one another; probably the property of forming lakes with mordants is dependent upon this structure. The dioxyanthraquinones isomeric with alizarin, *e.g.*, **quinizarin** (1 : 4), **anthrarufine** (1 : 5), **chrysazine** (1 : 8), **anthraflavic acid** (2 : 6), do not possess dyeing properties.

We have now to consider a number of dyes which are derivatives of the oxyanthraquinones.

Alizarin Brown, α-nitroalizarin ($OH : OH : NO_2 = 1 : 2 : 4$), is produced by nitrating alizarin in fuming sulphuric acid or in sulphuric acid containing arsenic acid, or by nitrating mono- or di-benzoylalizarin in sulphuric acid; nitration of alizarin in sulphuric acid containing boric acid gives **Alizarin Orange**, β-nitroalizarin ($OH : OH : NO_2 = 1 : 2 : 3$); nitration of flavopurpurin gives **Alizarin Orange G** ($OH : OH : OH : NO_2 = 1 : 2 : 6 : 3$). Reduction of α-nitroalizarin gives α-aminoalizarin, **Alizarin Garnet R**; **Alizarin Maroon** is a mixture of aminoalizarin and aminopurpurins, and is produced by nitrating commercial alizarin and then reducing.

Sulphonation of alizarin gives alizarin monosulphonic acid, **Alizarin Red S** ($OH : OH : SO_3H = 1 : 2 : 3$). Sulphonation of flavopurpurin gives **Alizarin Red 3WS** ($OH : OH : OH : SO_3H = 1 : 2 : 6 : 3$).

The above simple nitro-, amino-, and sulphonic derivatives are also mordant dyes.

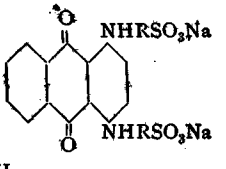
The bodies next to be discussed are acid wool dyes dyeing without mordants, though some can be subsequently chromed.

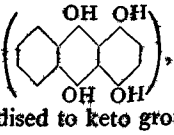
Alizarin Saphirol B, diaminoanthrarufin disulphonic acid, is produced by sulphonating anthrarufin, nitrating, and finally reducing.

Sulphonation and nitration of anthrachrysone (1 : 3 : 5 : 7-tetraoxyanthraquinone) gives **dinitroanthrachrysone disulphonic acid** dyeing brown shades; reduction gives the corresponding diamino bodies which dye violet; boiling the last named with alkali gives a hexaoxyanthraquinone disulphonic acid, Acid **Alizarin Blue BB** and **GR**.

An important property of the anthraquinone derivatives is the readiness with which negative substituents (Br, Cl, NO_2, OH, SO_3H) and also amino groups can be replaced by substituted amino groups NHR, where R is an alkyl or aryl radical. This reaction is applied in the production of a number of wool dyes; for example, quinizarin when condensed with aniline, *p*-toluidine, etc., gives—

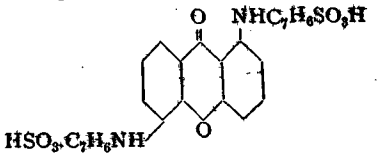
Sulphonation of these compounds gives **Quinizarin Greens**—



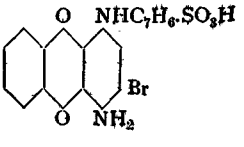
Leuco Quinizarin,  , gives the same products, the two meso-hydroxy groups being reoxidised to keto groups.

Other dyes of this type are—

Anthraquinone Violet—

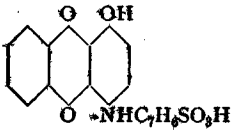


Alizarin Pure Blue—

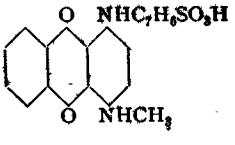


Alizarin Cyanine Green—

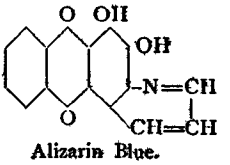
Alizarin Irisol—



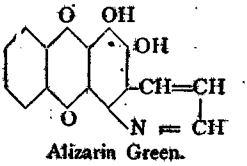
Alizarin Astrol—



Another type of anthraquinone derivative is that in which a nitrogen-containing ring is added to the anthracene nucleus—the **anthraquinolines**; these are obtained from nitro- or amino-oxyanthraquinones by Skraup's quinoline synthesis, viz., by treating these bodies with glycerol and sulphuric acid; in this manner β-nitro- or β-aminoalizarin gives **Alizarin Blue**, while α-aminoalizarin gives **Alizarin Green**—



Alizarin Blue.



Alizarin Green.

Both these compounds give soluble bisulphite compounds, **Alizarin Blue S** and **Alizarin Green S**, on treatment with sodium bisulphite, which are used in printing with chrome mordants.

A similar quinoline compound, **Alizarin Black P**, and its bisulphite combination, **Alizarin Black S**, are obtained from β-nitro- or β-amino-flavopurpurin.

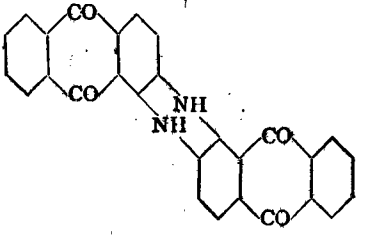
Treatment of Alizarin Green with strong sulphuric acid at high temperatures produces a 1 : 2 : 5 : 7 : 8-pentaoxyanthraquinoline, **Alizarin Indigo Blue**, which also gives a soluble bisulphite compound, **Alizarin Indigo Blue S**; concentrated or fuming sulphuric acid with Alizarin Blue gives 1 : 2 : 5 : 8-tetraoxyanthraquinoline, **Alizarin Green**, bisulphite compound **Alizarin Green S**.

Recent Developments in Anthracene Dyes—Anthracene Vat Dyes

In recent years there has been a great development in the anthracene dyes, chiefly in the production of the so-called "vat" dyes, *i.e.*, dyes which, like indigo, are insoluble, or practically so, in water, but yield on reduction colourless or slightly coloured "leuco" compounds which are soluble in alkali. The fabric to be dyed is impregnated with a solution of the leuco compound, and the dye is developed by oxidation in air or otherwise.

Vat Dyes derived from Anthracene.—The oldest anthracene vat dye is **Indanthrene, Indanthrene Blue R**, which is prepared by melting 2-amino-anthraquinone with caustic alkali (B.A.S.F., English Patents, 3,239, 1901; 22,762, 1901).

Indanthrene is N-dihydro-1 : 2 : 1′ : 2′-anthraquinoneazine—



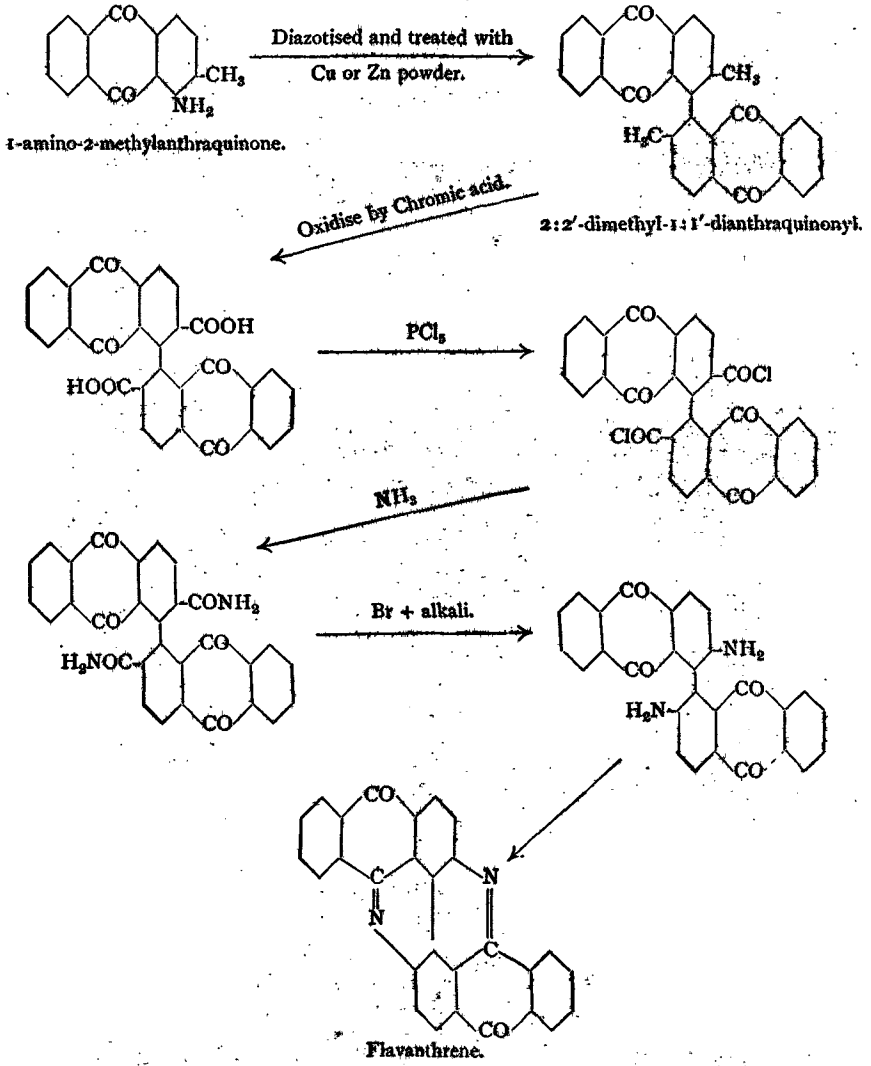
and dyes blue shades.

Indanthrene can also be prepared by condensing 1-amino-2-halogenanthraquinone (or 2-amino-1-halogenanthraquinone) with itself (F. v. Bayer, English Patent, 7,692, 1904); by condensing 1 : 2-diaminoanthraquinone with 1 : 2-anthraquinone and oxidising the product (F. v. Bayer, English Patent, 12,756, 1905); by condensing 1 : 2-diaminoanthraquinone with alizarin (F. v. Bayer, English Patent, 9,102, 1906); and together with Flavanthrene (*v. infra*) by treating 1-aminoanthraquinone with acid condensing agents (B.A.S.F., English Patent, 19,322, 1906). Halogenised indanthrenes (**Indanthrene Blue GC, GCD**, and **CE**, etc.) are prepared by chlorinating or brominating indanthrene (B.A.S.F., English Patents, 4,035 1902; 23,179, 1903; 17,242, 1905). **Algol Blue K** (N-dimethylindanthrene) is made from 1-methylamino-2-bromanthraquinone by the second method mentioned above.

Indanthrene disulphonic acid (B.A.S.F., English Patent, 12,185, 1901) and monosulphonic acid (B.A.S.F., English Patent, 339, 1909) are also known, as well as other derivatives.

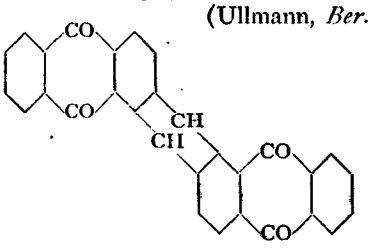
Another azine dye is **Flavanthrene** (Indanthrene Yellow) prepared by heating 2-aminoanthraquinone with alkali at a higher temperature than that required for Indanthrene; oxidising agents, *e.g.*, potassium nitrate, may be added to the melt; it is also obtained by heating 2-aminoanthraquinone with condensing agents, for instance, antimony pentachloride in nitrobenzene, or aluminium chloride alone, or by the action of acid oxidising agents, such as bichromate and sulphuric acid, manganese dioxide and sulphuric or nitric acid or lead peroxide (B.A.S.F., English Patent, 24,354, 1901). Flavanthrene dyes cotton blue shades which on standing become a bright yellow.

The following synthesis by Scholl (*Ber.*, 40, p. 1691) shows its constitution :—



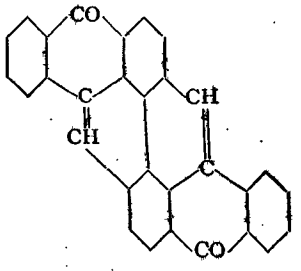
Analogous to Indanthrene and Flavanthrene, but containing methine groups in place of nitrogen, are **Anthraflavone** and **Pyranthrone**.

Anthraflavone—or the stilbenze derivative $C_{14}H_7O_2.CH=CH.C_{14}H_7O_2$ (Ullmann, *Ber.*, 46, 712).



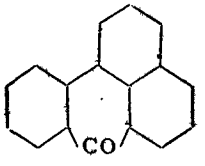
is prepared by treating 2-methylanthraquinone or its ω-halogen derivatives with condensing agents (B.A.S.F., English Patent, 10,677, 1905; D.R.P., 199,756); it dyes citron-yellow shades.

Pyranthrone (Indanthrene Gold Orange)—



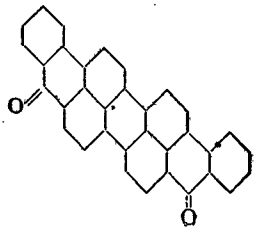
is prepared by treating 2:2'-dimethyl-1:1'-dianthraquinonyl with alkali or zinc chloride, with or without oxidation (B.A.S.F., English Patent, 14,578, 1905; Scholl, *Ber.*, 43, p. 346); it dyes orange tints. Treatment with halogens (English Patents, 10,505, 1906; 12,568, 1909) gives redder dyes.

The next group of dyes to be considered are the **benzanthrone** dyes. The benzanthrones are compounds containing the group—

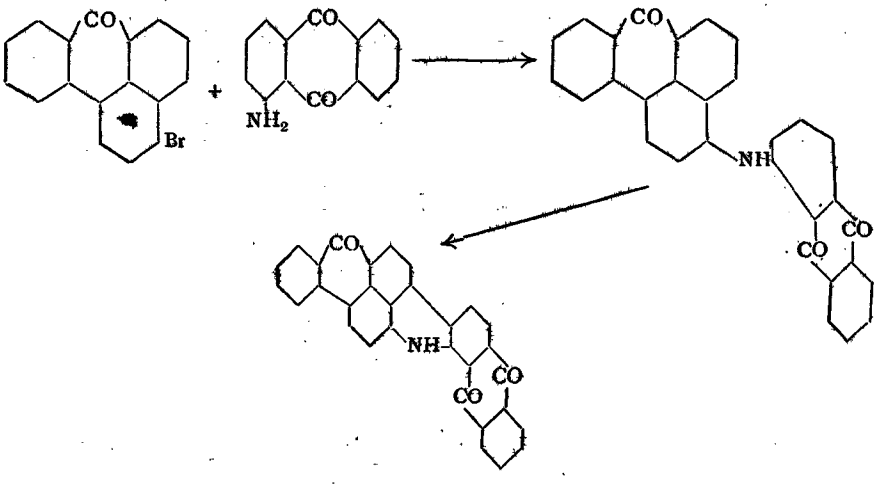


and are prepared by heating anthraquinone or its reduction products (anthranol, oxanthranol, or anthracene) or its amino, sulphonic, etc., derivatives with glycerin, preferably in presence of condensing agents, such as sulphuric acid. The benzanthrones undergo further condensation on being melted with alkalis, and yield blue to violet dyes (B.A.S.F., English Patent, 16,538, 1904; D.R.P., 176,018; Bally, *Ber.*, 38, p. 194).

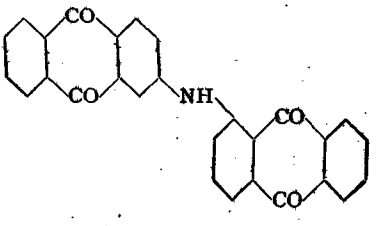
The dye prepared from anthranol is known as **Violanthrene**, and that obtained from 2-aminoanthraquinone as **Cyananthrene**. Violanthrene has the formula of a dibenzanthrone (see English Patent, 16,271, 1910)—



Among the derivatives of benzanthrone we may note: **benznaphthanthrone** from naphthanthraquinone (English Patent, 853, 1905) gives a reddish blue dye; **benzanthronequinolines** from α-aminoanthraquinones (English Patent, 3,819, 1905) give violet-blue dyes; green dyes (**Indanthrene Green, etc.**) by nitrating benzanthrone dyes, with or without subsequent reduction (English Patent, 1,818, 1905); halogen derivatives from halogenanthraquinones (English Patent, 7,022, 1905), or by halogenising the dyes (English Patent, 22,519, 1905); the latter dye violet-blue to red-violet shades. Halogenised benzanthrones, on treatment with alkali, give dyes which usually contain no halogen, and are known as **isoviolanthrenes** (English Patent, 20,837, 1905). Other derivatives are obtained by heating aminobenzanthrones with metallic salts or oxides (English Patents, 10,770, 1907; 3,156, 1908). Brombenzanthrone condensed with 1-aminoanthraquinone gives benzanthronyl-1-aminoanthraquinone, which, by treatment with condensing agents, gives a **green dye** (English Patent, 24,604, 1908; D.R.P., 212,471).



Another group of dyes is that containing two or three anthraquinone nuclei united by NH groups, the **dianthraquinonylamines** and **trianthraquinonylamines**, **α-β-Dianthraquinonylamine** (Algol Orange R)—



is prepared by condensing 2-aminoanthraquinone with 1-chloranthraquinone, or 1-aminoanthraquinone with 2-chloranthraquinone (D.R.P., 162,824; B.A.S.F., English Patent, 19,199, 1905); it dyes orange shades (F. v. Bayer, English Patent, 24,810, 1908).

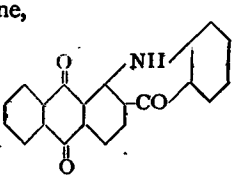
Trianthraquinonylamines, dyeing red shades, are produced by condensing two molecular proportions of 2-chloranthraquinone with 1 : 5-diaminoanthraquinone (**Indanthrene Bordeaux B**, B.A.S.F., English Patent, 10,324, 1906), or by condensing two molecular proportions of 1-aminoanthraquinone with β-β-dihalogenanthraquinones (**Indanthrene Red G**, B.A.S.F., English Patent, 4,235, 1907). A number of derivatives of di- and tri-anthraquinonylamines giving a variety of shades are known (English Patents, 10,860, 1906; 13,057, 1906; 7,418, 1908; 12,167, 1908; 5,382, 1909; 9,219, 1909).

A further group of dyes is the **acidylaminoanthraquinones**, obtained by introducing the formyl, acetyl, benzoyl, succinyl, salicylyl, thiosalicylyl, anisyl, cinnamyl, etc., radicals into the amino groups of aminoanthraquinones (F. v. Bayer, English Patents, 2,709, 1909; 3,055, 1909); these dye yellow, red, orange, blue, violet, etc., shades (**Algol Yellows, Algol Reds**, etc.). **Helindon Yellow 3GN** (English Patent, 24,920, 1909), is a symmetrical urea derived from 2-aminoanthraquinone.

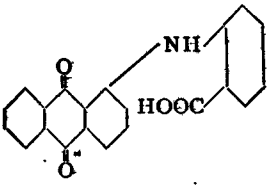
A number of anthracene vat dyes containing sulphur are also known, *e.g.*, **mercaptans** (English Patent, 10,387, 1908), **thiazoles** (English Patent, 12,828, 1911), **thiazines** (English Patents, 18,240, 1911; 28,479, 1911), **thioureas** (English Patent, 11,473, 1910).

Two groups of dyes which are at present attracting attention are the **anthraquinone acridones** and **thioxanthones**.

Anthraquinone 1 : 2-acridone,

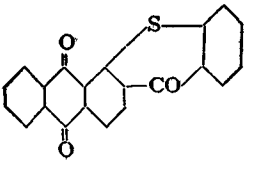


is prepared by condensing anthranilic acid with *a*-chlor- or *a*-nitro-anthraquinone and heating the resulting carboxyanilido-anthraquinone,



with condensing agents (Ullmann, English Patent, 12,653, 1909).

Anthraquinone- 1 : 2-thioxanthrone,



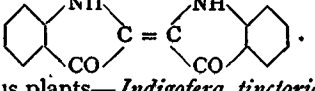
is similarly prepared from thiosalicylic acid (Ullmann, English Patent, 30,480, 1909).

A number of derivatives of these dyes have been prepared (B.A.S.F., English Patent, 13,907, 1909, etc.).

3. DYES OF THE INDIGO, THIOINDIGO, AND INDIGOID SERIES

Indigo (Indigo Blue, Indigotin)

Is the most important dye of commerce. It was originally obtained from natural sources, but the natural indigo has been very largely replaced by synthetic indigo, the manufacture of which is perhaps the greatest triumph of dyestuff chemistry.

Indigo has the formula, $C_{16}H_{10}N_2O_2$, or  . It occurs in nature as a glucoside, **indican**, in various plants—*Indigofera tinctoria, Indigo anil, Polygonium tinctorium, Isatis tinctoria.* Hydrolysis of the indican gives indigo and a sugar, indiglucin; this hydrolysis is effected in practice by fermenting the leaves and stems of the indigo-bearing plants.

Indigo has been synthesised by a number of processes, only the more important of which can be dealt with here.

Baeyer in 1880 synthesised it from *o*-nitrocinnamic acid, $C_6H_4\begin{cases}CH{=}CH.COOH\\NO_2\end{cases}$. Treatment of this compound with bromine gives *o*-nitrodibromhydrocinnamic acid, $C_6H_4\begin{cases}CHBr{-}CHBr.COOH\\NO_2\end{cases}$, from which alkalis remove hydrobromic acid, giving *o*-nitrophenylpropiolic acid, $C_6H_4\begin{cases}C{\equiv}C.COOH\\NO_2\end{cases}$; this compound, on treatment with alkaline reducing agents, splits off carbon dioxide and condenses to indigo. An alternative method consists in treating *o*-nitrocinnamic acid with chlorine, which gives phenylchlorlactic acid, $C_6H_4\begin{cases}CHOH{-}CHCl.COOH\\NO_2\end{cases}$; alkalis convert this compound into *o*-nitrophenyloxyacrylic acid, $C_6H_4\begin{cases}O\\CH{-}CH.COOH\\NO_2\end{cases}$, which condenses on heating in solution into indigo.

In 1882 Baeyer synthesised indigo from *o*-nitrobenzaldehyde; treatment of this body with acetone gives *o*-nitrophenyllactomethylketone, $C_6H_4\begin{cases}CHOH.CH_2COCH_3\\NO_2\end{cases}$, which is converted into indigo by treatment with alkalis. These syntheses of Baeyer's were not, however, a commercial success, although *o*-nitrophenyllactomethylketone has been employed under the name of Indigo salt for producing indigo on the fibre (the bisulphite compound of the ketone being printed on the fibre which is then passed through an alkaline bath).

Heumann's synthesis of indigo in 1890 from phenylglycine, and soon afterwards from phenylglycine-*o*-carboxylic acid, led to the commercially successful placing of synthetic indigo upon the world's markets.

Two main processes are now worked on a very large scale:—

1. **The Phenylglycine Process**, worked by the Höchst Farbwerke, consists in heating aniline with chloracetic acid, when phenylglycine is formed, thus:—

$$\underset{\text{Aniline.}}{C_6H_5.NH_2} + \underset{\text{Chloracetic acid.}}{Cl.CH_2.COOH} = \underset{\text{Phenylglycine.}}{C_6H_5.NH.CH_2.COOH} + HCl.$$

(Phenylglycine has also been made by heating aniline with HCN and formaldehyde.) The phenylglycine is next melted with caustic soda to form indoxyl, $C_6H_5\begin{cases}NH\\CO\end{cases}CH_2$ or $C_6H_5\begin{cases}NH\\C(OH)\end{cases}CH$, thus:—

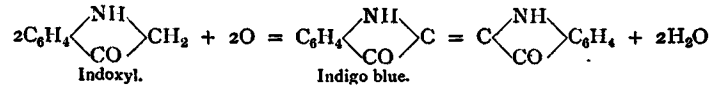
$$\underset{\text{Sodium salt of phenylglycine.}}{C_6H_5.NH.CH_2.COONa} + NaOH = C_6H_4\begin{cases}NH\\CO\end{cases}CH_2 + 2NaOH.$$
$$\text{Indoxyl.}$$

But since at the high temperature necessary for proper fusion a large portion of the parent materials are destroyed by the alkali, with a resulting poor yield of indoxyl, it is preferable to add materials to the caustic soda to lower the temperature of melting. A great improvement was effected by the Frankfurter Scheideanstalt by adding sodamide, $NaNH_2$ (M.P. 120° C.; prepared by heating metallic sodium in a stream of dry NH_3, see p. 638), when the following change takes place:—

$$\underset{\text{Phenylglycine.}}{C_6H_5.NH.CH_2.COOH} + \underset{\text{Sodamide.}}{Na.NH_2} = C_6H_4\begin{cases}NH\\CO\end{cases}CH_2 + NaOH + NH_3.$$
$$\text{Indoxyl.}$$

The escaping ammonia is collected and used again. Carbides and nitrides have also been used instead of sodamide. To obtain indigo the melt is dissolved in water, and air blown through to oxidise and condense the indoxyl (probably present in the alkaline solution as the sodium salt, $C_6H_4\begin{cases}NH\\C(ONa)\end{cases}CH$) to indigo;

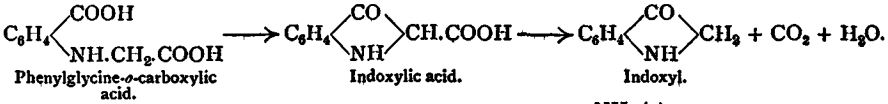
or the solution is acidified so as to give free indoxyl, which is then oxidised and condensed to indigo :—



Indoxyl. Indigo blue.

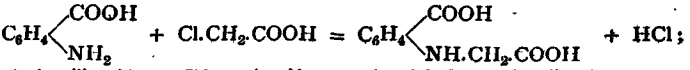
In this process the starting point is benzene (from which aniline is obtained by nitrating and reducing as described on p. 424), while intermediately chloracetic acid, caustic soda, and sodamide are used. The success of the synthesis depends entirely upon the price at which these materials are obtainable.

2. **The Phenylglycine-*o*-Carboxylic Acid Process,** worked by the Badische Anilin- und Soda-Fabrik, depends upon the fact that when phenylglycine-*o*-carboxylic acid is melted with caustic alkalies, it condenses, thus :—



Phenylglycine-*o*-carboxylic acid. Indoxylic acid. Indoxyl.

The starting point in this process is **Anthranilic Acid,** $C_6H_4\begin{matrix}NH_2\ (1)\\COOH\ (2)\end{matrix}$, which the B.A.S.F. obtain from the cheap and abundant naphthalene by the following series of operations: (1) The naphthalene is oxidised to phthalic acid, $C_6H_4(COOH)_2$, by heating with concentrated sulphuric acid and mercury (see **Phthalic Acid,** p. 430), when the anhydride of the acid distils over; (2) the phthalic anhydride, $C_6H_4\begin{matrix}CO\\CO\end{matrix}O$, thus obtained is converted into phthalimide, $C_6H_4\begin{matrix}CO\\CO\end{matrix}NH$, by heating with ammonia; which (3) on treating with bleaching powder or NaOCl gives anthranilic acid, $C_6H_4(COOH).(NH_2)$ (see p. 430); (the anthranilic acid may also be obtained by heating *o*-chlorbenzoic acid, $C_6H_4.Cl.COOH$ (1 : 2) with NH_3 in the presence of Cu); (4) next, the anthranilic acid is treated with chloracetic acid to obtain phenylglycine-*o*-carboxylic acid—



Anthranilic acid. Chloracetic acid. Phenylglycine-*o*-carboxylic acid.

and (5) the phenylglycine-*o*-carboxylic acid is finally converted into indoxyl and then into indigo as above described.

It has also been shown that for phenylglycine-*o*-carboxylic acid one may substitute methyl-anthranilic acid, $C_6H_4\begin{matrix}COOH\\NH.CH_3\end{matrix}$, when melting with sodamide for indoxyl. According to this latter process the use of chloracetic acid is abolished, since methylanthranilic acid may be produced directly from anthranilic acid by treating with methyl chloride, or from phthalic anhydride by treating with methylamine.

On comparing the two main processes for manufacturing synthetic indigo, it will be seen that the one starts from benzene, and the other from naphthalene. Both processes at present work with monochloracetic acid, thereby creating a huge demand for glacial acetic acid (about 3,000 tons are used annually, being obtained from the distillation of about 150,000 cub. yds. of wood). The chlorine for chlorinating the acetic acid is obtained by electrolysing alkali chlorides, which also produces caustic alkali. Finally the demand for a concentrated sulphuric acid for oxidising naphthalene to phthalic acid, coupled with the escape of large amounts of SO_2 and SO_3 during the heating process, contributed very essentially to the industrial development of the contact process for the manufacture of sulphuric acid. The manufacture of synthetic indigo thus furnishes a very interesting series of examples of the interaction of one branch of chemical industry on others.

The following statistics show that although **synthetic indigo** has largely diminished the culture of **natural indigo** in India and other tropical countries, yet the demand for indigo is also not increasing, probably owing to the competitive action of several very fast blue dyes, derived from anthracene, which are now on the market.

Imported into Great Britain:—

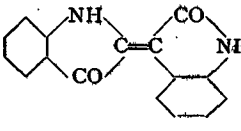
	1896.	1906.	1907.	1908.	1909.	1913.	Value. (1913).
		Cwt.	Cwt.	Cwt.	Cwt.	Cwt.	
Synthetic indigo	0	39,042	41,379	37,761	33,494	23,889	£76,695
Natural indigo	...	7,641	11,116	8,644	10,051	4,174	54,739

Practically all the synthetic indigo imported into Great Britain comes from Germany: (1910) **Germany**, 28,182 cwt. (value, £101,183); **Netherlands**, 4 cwt. (value, £16); **Belgium**, 10 cwt. (value, £50); **other countries**, *nil*. The total amount of synthetic indigo exported from Germany in 1909 amounted to 161,100 dz. = 16,110 metric tons, or roughly, 320,000 cwt. representing a value of 40.3 million marks (say £2,000,000).

The United States imported of Indigo: 1906, 7,393,000 lbs.; 1910, 7,539,000 lbs.; value in 1910, $1,196,000. Of this quantity Germany imports 7,000,000 lbs., value $1,000,000.

Indigo is a typical vat dye, *i.e.*, before dyeing it is reduced to its leuco compound, indigo white, $C_6H_4\langle^{NH}_{C(OH)}\rangle C{=}C\langle^{NH}_{C(OH)}\rangle C_6H_4$, which is soluble in alkalies; the fibre (cotton, wool, or silk) is immersed in an alkaline solution of this body, and is then withdrawn and oxidised to indigo by exposure to air. The old method of obtaining the vat was by fermentation by means of dung; other methods consisted in the use of glucose and alkali, lime and ferrous sulphate, or zinc and alkali; the vat is now usually prepared by means of sodium hydrosulphite and alkali.

Indirubin or Indigo Red is an isomer of indigo and has the constitution



It occurs as an impurity in natural indigo, and may be prepared by the condensation of indoxyl with isatin, $C_6H_4\langle^{NH}_{CO}\rangle CO$; it is of no value as a dye.

Sulphonation of indigo yields a disulphonic acid, **Indigo Carmine**, which is an acid wool dye.

Halogenised Indigo Dyes

Halogenised indigo dyes, *i.e.*, indigo derivatives in which one or more of the hydrogen atoms of the benzene nuclei has or have been replaced by bromine or chlorine, may be prepared by two general methods:—

1. Treatment of indigo or a derivative thereof, either alone or suspended or dissolved in various media, with halogen or with halogenising agents.

2. Obtaining a halogenised parent material, *e.g.*, brom- or chlor-phenylglycine-*o*-carboxylic acid, which is then subjected to suitable treatment, say condensation and oxidation, to yield a halogenised dye.

These two methods have been known for some years, but until 1907 had only been applied to the production of mono- and di-halogen derivatives, except as regards a tetrachlorindigo prepared in 1901 from dichlorinated phenylglycine-*o*-carboxylic acid (B.A.S.F., English Patent, 20,552, 1901).

From 1907 onwards both methods have been largely extended, and halogen-indigos containing from 3 to 6 atoms of halogen in the molecule are now known.

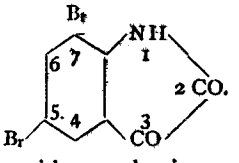
By treating indigo, suspended in an inert medium such as nitrobenzene, with the theoretical amount of bromine (two atomic proportions of bromine for each bromine atom to be introduced into the indigo molecule), at a raised temperature, **tri-** and **tetra-bromindigos** are obtained (S.C.I.B., English Patent, 5,122, 1907; D.R.P., 193,438). By applying this method to mono- and di-chlorindigos, mixed tri- and tetra-halogenindigos are produced, and from the para-dihalogenindigos (*i.e.*, containing halogen in para position to the carbonyl group) penta- and hexa-halogenindigos result (S.C.I.B., English Patent, 10,326, 1907).

Chlorination of indigo in similar media in presence of chlorine carriers yields **tri-** and **tetra-chlorindigos** (S.C.I.B., English Patent, 19,793, 1908).

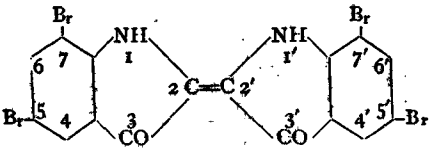
The above-described products dye reddish-blue shades.

The constitution of these bodies has been established by Grandmougin (*Ber.*, 42, p. 4408) in the following way:—

Tetrabromindigo obtained by bromination in nitrobenzene is oxidised by means of nitric acid to a dibromisatin of M.P. 249°-250° C., which is identical with the known 5 : 7-dibromisatin,



Distillation of the dibromisatin with potash gives 2 : 4-dibromaniline. The tetrabromindigo is, therefore, 5 : 7 : 5′ : 7′-tetrabromindigo,



The nomenclature here employed is that of Friedländer (*Ber.*, 42, p. 765). The di- and tri-bromindigos obtained similarly are the 5 : 5′ and 5 : 7 : 5′ bodies. The tetrabromindigo is known in commerce as **Ciba Blue.***

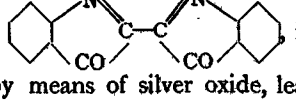
Another method of bromination consists in treating indigo suspended in concentrated sulphuric acid with bromine in the cold (F. v. Bayer, English Patent, 4,423, 1908). In this process the hydrobromic acid formed is partly oxidised by the sulphuric acid, so that less than the theoretical amount of bromine can be used; for the same reason bromides may be used instead of bromine in this process (F. v. Bayer, English Patent, 5,582, 1908). The tri- and tetra-bromindigos so obtained dye greenish-blue shades. Grandmougin asserts that they are identical with the products obtained by bromination in nitrobenzene (*Ber.*, 43, p. 937). A closely allied process is that of Kalle & Co. (English Patent, 15,088, 1909), in which chlorsulphonic acid is used as the suspension medium during the bromination.

Another process (F. v. M.L.B., English Patent, 25,513, 1907) consists in treating dihalogenindigos with excess of bromine alone; greenish black products are thus obtained which appear to be perbromides of bromindigos; treatment of these bodies with sodium bisulphite removes the loosely combined bromine, giving the brominated dyes. Similar perbromides are obtained by using excess of bromine in presence of concentrated sulphuric acid (English Patent, 25,514, 1907).

The above-described processes—bromination in sulphuric or chlorsulphonic acid, or with bromine alone—can also be applied to produce **penta-** and **hexa-bromindigos** (English Patents, 13,789, 1908; 2,609, 1909; 3,019, 1909), which also dye greenish blue shades.

According to Grandmougin (*Ber.*, 43, p. 937) the penta- and hexabromindigos obtained by bromination in sulphuric acid are the 4 : 5 : 7 : 5′ : 7′ and 4 : 5 : 7 : 4′ : 5′ : 7′ bodies respectively.

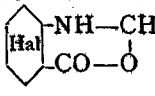
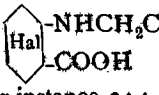
An interesting process is that of Kalb in which dehydroindigo forms the starting point (*Ber.*, 42, p. 3642 *et seq.*, p. 3653 *et seq.*; B.A.S.F., English Patents, 16,377, 1909; 22,714, 1909).

Dehydroindigo,  , is obtained by careful oxidation of indigo, for instance by means of silver oxide, lead dioxide, manganese dioxide, or

* The trade names are here given on the authority of Bohn, *Ber.*, 43, p. 987.

permanganates, in absence of water, and in presence of indifferent diluents, *e.g.*, chloroform, benzene, or nitrobenzene. If anhydrous acids are also present the corresponding dehydroindigo salts are formed. Dehydroindigo is also formed by treating indigo with halogen or halogenising agents under suitable conditions. With sodium sulphite or bisulphite, dehydroindigo forms soluble compounds, which can be readily halogenised by treatment with chlorine or bromine, even in presence of water; the tetrahalogen bodies thus produced are the 5:7:5′:7′ bodies. The other salts of dehydroindigo can be halogenised similarly; on reduction they yield the halogenindigos.

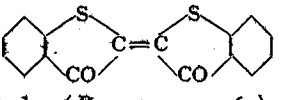
The unsymmetrical condensation product from isatin and indoxyl, indirubin, has been brominated by various processes; mono- to hexa-brom derivatives, dyeing reddish blue shades, have thus been obtained (S.C.I.B., English Patents, 6,106, 1907; 8,530, 1908; 6,351, 1910). The **tetra-bromindirubin** is known as **Ciba Heliotrope.**

Under the second method we may note two processes of the B.A.S.F. (English Patents, 6,991, 1909, and 6,992, 1909). According to the first of these a halogenised anthranilic acid is treated with formaldehyde, giving a compound of the formula  ; this on treatment with a cyanide gives the corresponding ω-cyanmethylanthranilic acid,  , which is saponified to halogenphenylglycine-*o*-carboxylic acid, for instance 3:4-, 4:5-, and 4:6-dihalogenphenylglycine-*o*-carboxylic acid. The 4:6-dichlorphenylglycine-*o*-carboxylic acid thus prepared is identical with that prepared by chlorinating phenylglycine-*o*-carboxylic acid (English Patent, 20,552, 1901), and the tetrachlorindigo of this last-mentioned Patent is, therefore, the 5:7:5′:7′ body. According to the second Patent, No. 6,992, 1909, dihalogenphenylglycine-*o*-carboxylic esters are used as parent materials; by this process the 5:7:5′:7′-, 4:5:4′:5′-, 4:4′:6:6′-, and 5:5′:6:6′-tetrachlorindigos and the 4:4′-dichlor-5:5′-dibrom- and 5:5′-dichlor-7:7′-dibromindigos have been prepared.

In connection with the halogenindigos it is noteworthy that the ancient **Tyrian purple** obtained from *Murex Brandaris* has been shown by Friedländer (*Ber.*, 42, p. 765) to consist essentially of 6:6′-dibromindigo.

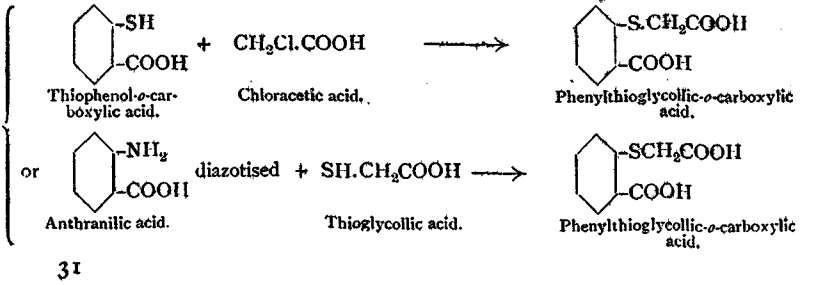
Thioindigo Dyes

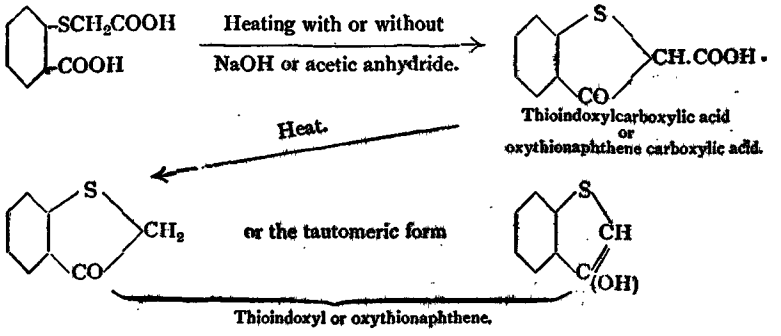
Thioindigo is an analogue of indigo containing sulphur in place of the NH groups—



It was discovered by Friedländer (*Ber.*, 39, p. 1060) and first put on the market as Thioindigo Red B by Kalle & Co. (English Patents, 22,736, 1905; 23,316, 1905; 14,261, 1906; 16,100, 1906; 16,101, 1906).

The process for its production is shown by the following scheme:—





Condensation and oxidation of this latter body gives thioindigo.

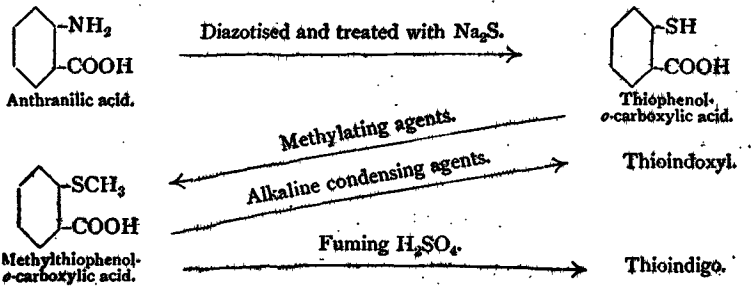
It will be seen that this process corresponds with the Heumann synthesis of indigo from phenylglycine-*o*-carboxylic acid.

This synthesis has been followed by the production of a large number of derivatives of thioindigo and allied dyes. The following general methods may be noted:—

2. Treatment of arylthioglycollic acids or their salts or esters, $RSCH_2COOR_1$, with acid condensing agents, such as sulphuric acid, phosphorus pentoxide, acetic anhydride, zinc chloride, potassium bisulphate, or oxalic acid, and oxidation of the resulting thioindoxyl derivatives (B.A.S.F., English Patent, 28,578, 1906).

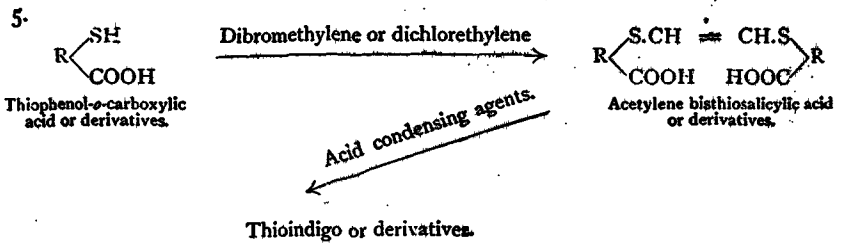
3. Conversion of arylthioglycollic acids into the acid chlorides, $RSCH_2COCl$, by means of phosphorus tri- or pentachloride or oxychloride; the acid chlorides on treatment with aluminium chloride give thioindoxyl derivatives (B.A.S.F., English Patent, 14,191, 1906).

4.



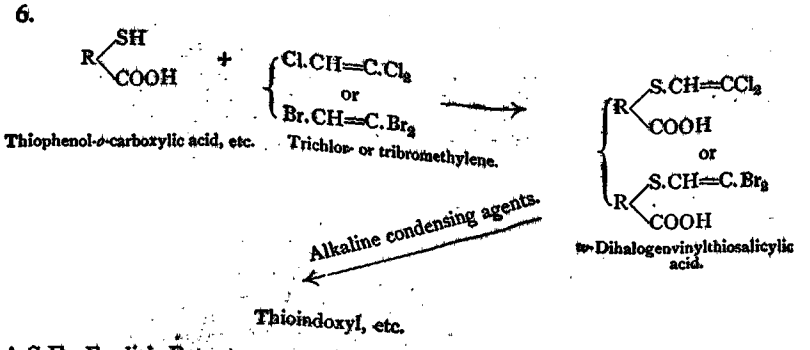
(F. v. M.L.B., English Patent, 593, 1907.)

5.



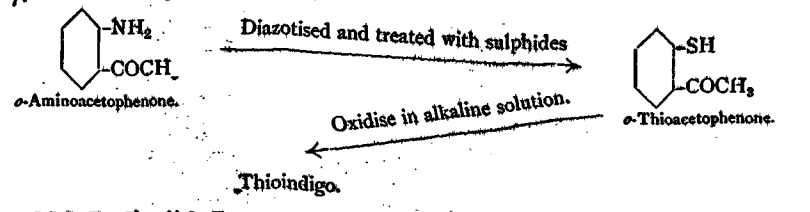
(B.A.S.F., English Patent, 26,053, 1907.)

6.

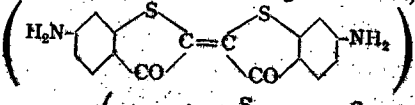
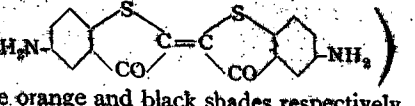


(B.A.S.F., English Patent, 90, 1908.)

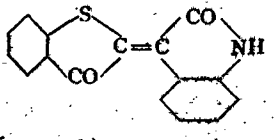
7.



(F. v. M.L.B., English Patent, 4,541, 1908.)

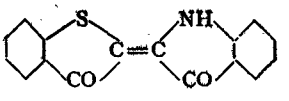
Among the **derivatives of thioindigo** we may note the following: Halogen derivatives obtained from halogenised parent materials or by halogenising the dyes, as in the case of indigo (S.C.I.B., English Patent, 6,490, 1907); alkyloxy and alkylthio derivatives (F. v. M.L.B, English Patent, 1,472, 1907); amino derivatives (F. v. M.L.B., English Patent, 16,584, 1907). The *m*-amino compound  dyes brown shades, and the *p*-amino compound  black shades; their halogen derivatives dye orange and black shades respectively.

Unsymmetrical dyes containing only one thionaphthene residue have also been prepared. The condensation of thioindoxyl with isatin gives **Thioindigo Scarlet R**, the analogue of indirubin—



(Kalle, English Patent, 17,162, 1906.)

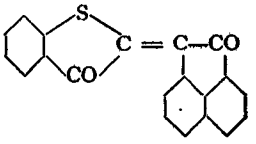
Condensation of thioindoxyl with α-isatinanilide gives **Ciba Violet A**—



(S.C.I.B., English Patent, 11,760, 1906.)

The same product is obtained from α-isatin chloride and thioindoxyl (Kalle, English Patent, 11,609, 1907.)

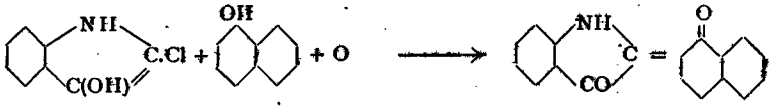
Condensation of thioindoxyl with acenaphthenequinone gives **Ciba Scarlet G**—



(S.C.I.B., English Patent, 344, 1908.)

Other Indigoid Dyes

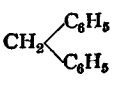
Friedländer (*Ber.*, 41, p. 772) has described dyes which contain half the indigo molecule, and may be termed indigoid dyes. They are obtained by condensing α-isatin derivatives with phenolic compounds such as 1-naphthol, 1-anthrol, or their derivatives. The reactions between α-isatin chloride and 1-naphthol may be given thus—



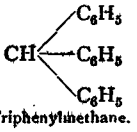
See also for these dyes, English Patents, 7,819, 1909 (Bayer); 3,206, 1910 (Kalle).

4. DI- AND TRIARYLMETHANE DYES

Under this heading are grouped a number of dyes, which may be regarded as derivatives of diphenylmethane and triphenylmethane—



Diphenylmethane.



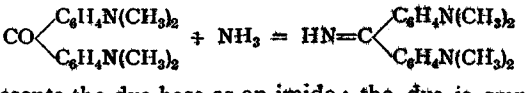
Triphenylmethane.

One or more of the phenyl groups may be replaced by naphthyl groups to give, *e.g.*, diphenylnaphthylmethane dyes.

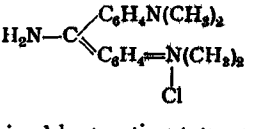
(*a*) Diphenylmethane Dyes

The only important dyes of this class are the **Auramines.**

Auramine is obtained by treating tetramethyldiaminobenzophenone with ammonia; the reaction may be expressed:—



This represents the dye base as an imide; the dye is employed in the form of its hydrochloride, which may be formulated either as the hydrochloride of the imide base, or as—



Auramine may also be obtained by treating tetramethyldiaminodiphenylmethane, $CH_2\langle^{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2}$, with sulphuric acid and then with ammonia.

The parent materials, tetramethyldiaminobenzophenone and tetramethyldiaminodiphenylmethane, are prepared by the action of phosgene and formaldehyde, respectively, on dimethylaniline (see pp. 434, 467).

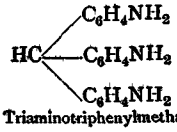
Auramine dyes wool, silk, or tannin-mordanted cotton bright yellow shades.

Auramine G is prepared similarly from dimethyldiaminoditolylmethane.

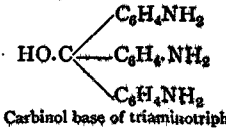
(*b*) Triphenylmethane Dyes

These may be divided broadly into two types: (1) those containing amino groups; (2) those containing hydroxy groups, with or without carboxylic groups. The first of these, which is the more important, may again be subdivided into dyes containing two amino groups (Malachite Green type) and dyes containing three amino groups (Rosaniline type).

Before discussing the individual dyes of these groups, it will be well to consider generally their constitution. There are three stages to be considered in the formation of the amino dyes—the leuco base, the carbinol base, and the dye itself. The leuco bases are the triphenylmethane derivatives—thus Paraleucaniline, the leuco base of Pararosaniline, is triaminotriphenylmethane; oxidation of this body gives the carbinol base—

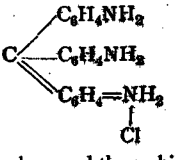


Triaminotriphenylmethane.



Carbinol base of triaminotriphenylmethane.

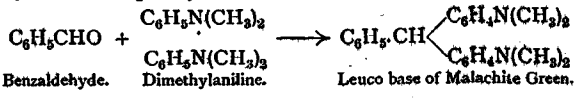
The dye **Pararosaniline** is the hydrochloride of this body, less the elements of water. Several formulæ are possible for such a body, and there has been considerable controversy as to the correct one. The balance of evidence appears to favour Nietzki's formula representing this body as quinonoid—*



It should be noted that both the leuco base and the carbinol base are colourless—it is only when the carbinol base is converted into a salt that the dye results.

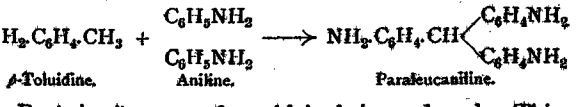
General Methods of Production

Triphenylmethane derivatives may be produced by a variety of processes. In each of these some compound must be present which will supply the methane carbon. Thus, for instance, benzaldehyde condenses with two molecules of dimethylaniline giving tetramethyldiaminodiphenylmethane, the leuco base of **Malachite Green**—



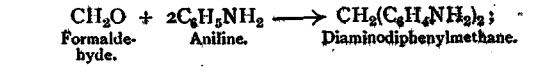
Benzaldehyde. Dimethylaniline. Leuco base of Malachite Green.

Or a methyl group attached to an aromatic nucleus may supply the methane carbon as in the production of Paraleucaniline (*v. supra*) by oxidising a mixture of *p*-toluidine and aniline:—



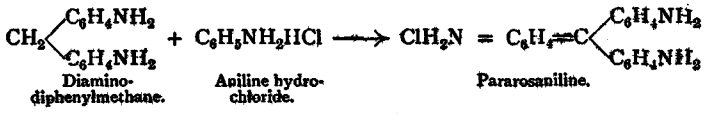
p-Toluidine. Aniline. Paraleucaniline.

In the "New Fuchsine" process formaldehyde is employed. This condenses with two molecules of aniline to form diaminodiphenylmethane, which is then oxidised together with aniline and aniline hydrochloride to give Pararosaniline—

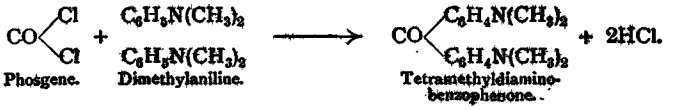


Formaldehyde. Aniline. Diaminodiphenylmethane.

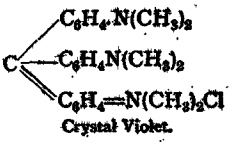
* For a summary of the evidence see Sidgwick's "Organic Chemistry of Nitrogen," Oxford, 1910, p. 61.



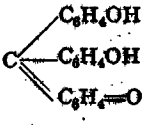
Phosgene, again, reacts with dimethylaniline to give tetramethyldiaminobenzophenone—



This may be converted into the chloride and condensed with a further molecule of dimethylaniline, or reduced to the benzhydrol, which is condensed with dimethylaniline and the leuco compound oxidised, giving **Crystal Violet**, hexamethyl pararosaniline hydrochloride—



Oxalic acid has also been employed, as in the manufacture of **Aurine** (trioxytriphenylcarbinol anhydride) from phenol, oxalic acid, and sulphuric acid. We may suppose that formic acid is first produced, which then reacts with the phenol, giving **Aurine**—



The preparation and properties of some typical triphenylmethane dyes are given below :—

Diamino Compounds (Malachite Green Series).

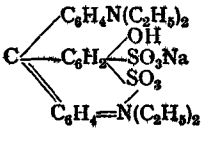
Malachite Green is essentially a salt of tetramethyldiaminotriphenyl carbinol. It usually appears in commerce as the zinc or iron double chloride, or the oxalate. Its method of preparation has already been indicated. It dyes wool, silk, and tannin-mordanted cotton green.

Brilliant Green is prepared similarly from benzaldehyde and diethylaniline; its dyeing properties are similar to those of Malachite Green.

Setoglaucine is prepared from *o*-chlorbenzaldehyde and dimethylaniline.

Setocyanine, Victoria Green 3B, and **Glacier Blue** are other dyes of this type.

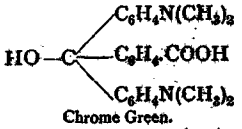
The above-described dyes are basic dyes; the sulphonic acids of this series are acid wool dyes. Examples are **Erioglaucine A,** from benzaldehyde-*o*-sulphonic acid and ethylbenzylaniline sulphonic acid, **Night Blue B,** from *o*-chlor-*m*-nitrobenzaldehyde and ethylbenzylaniline sulphonic acid;

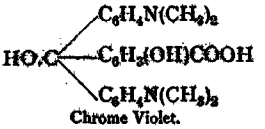


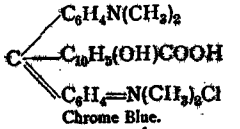
Patent Blue V is obtained by condensing *m*-oxybenzaldehyde with diethylaniline and sulphonating the product, or from *m*-nitrobenzaldehyde and diethylaniline, reducing and diazotising to form the hydroxy group, and sulphonating.

Patent Blue A is the corresponding product from ethylbenzylaniline.

The mordant dyes, **Chrome Green, Chrome Violet,** and **Chrome Blue,**


Chrome Green.


Chrome Violet.

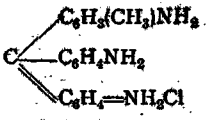

Chrome Blue.

are obtained from tetramethyldiaminobenzhydrol and benzoic, salicylic, or α-oxynaphthoic acid respectively, and may also be included in this class.

Triamino Compounds—Rosaniline Series.

Pararosaniline (Parafuchsine, Paramagenta) has already been referred to (pp. 467, 468).

Rosaniline (Fuchsine, Magenta) is the hydrochloride of triaminodiphenyltolylcarbinol—



and is prepared similarly either by oxidising a mixture of aniline and *o*- and *p*-toluidine by various oxidising agents, or by the New Fuchsine process from formaldehyde, aniline, and *o*-toluidine. **New Fuchsine** (hydrochloride of triaminotritolylcarbinol) is prepared from formaldehyde and *o*-toluidine.

These three dyes are basic dyes, dyeing wool, silk, and tannin-mordanted cotton red shades.

Rosaniline is one of the oldest synthetic dyes, having been put on the market in 1859 by Verguin. The constitution of this and Pararosaniline was not, however, ascertained until 1878 by E. and O. Fischer (see for example Georgevics, "Chemistry of Dyestuffs," p. 137). The alkylated, benzylated, and arylated rosaniline dyes are also basic dyes; they are obtained either by alkylating, etc., the rosanilines or by treating the corresponding tertiary amines according to the general processes indicated above. Examples are:—

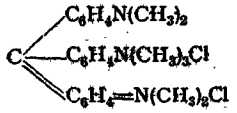
Hofmann Violet, a mixture of mono-, di-, and tri-methyl or -ethyl rosaniline and pararosaniline hydrochloride, from methyl or ethyl halides and rosaniline and pararosaniline.

Aniline Blue, spirit soluble, triphenylrosaniline and triphenyl-pararosaniline hydrochloride, by the action of aniline on impure rosaniline.

Methyl Violet, penta- and hexa-methyl-pararosaniline, by the oxidation of dimethylaniline.

Crystal Violet, from dimethylaniline (*v.* above).

Ethyl Violet, the corresponding dye from diethylaniline.



Methyl Green, heptamethylpararosaniline chloride, by acting on Methyl Violet with methyl chloride.

Ethyl Green, ethylhexamethyl pararosanilinechlorbromide, by treating Methyl Violet with ethyl bromide.

Benzyl Violet, obtained by acting on Methyl Violet with benzyl chloride.

The sulphonic acids of the rosaniline series are obtained either by sulphonating the basic dyes, or from the amine sulphonic acids. Typical examples are:—

Acid Magenta, a mixture of trisulphonic acids of rosaniline and pararosaniline obtained by sulphonation of the bases, dyes wool in acid baths.

Alkali Blue, monosulphonic acid of triphenylrosaniline and triphenylpararosaniline, obtained by sulphonation, dyes wool in an alkaline bath.

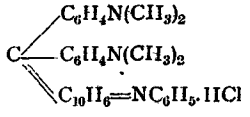
Soluble Blue is the corresponding trisulphonic acid, and dyes silk and mordanted cotton.

Höchst New Blue, a trisulphonic acid obtained by sulphonation of trimethyltriphenylpararosaniline (obtained from phosgene and methyldiphenylamine), dyes wool from acid baths.

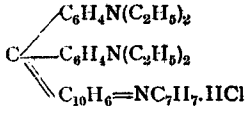
Acid Violet 6B, disulphonic acid of dimethyldiethyldibenzyltriaminotriphenylcarbinol, obtained from dimethyl-*p*-aminobenzaldehyde and ethylbenzylaniline sulphonic acid, dyes wool from acid baths.

Eriocyanine A, tetramethyldibenzylrosanilinedisulphonic acid, from tetramethyldiaminobenzhydrol sulphonic acid and dibenzylaniline sulphonic acid, dyes wool reddish blue in acid baths.

We may include here the triaminodiphenylnaphthylmethane dyes:—



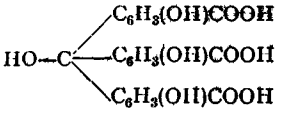
Victoria Blue B is obtained from phenyl-α-naphthylamine and tetramethyldiaminobenzophenone chloride or tetramethyldiaminobenzhydrol. It dyes wool, silk, or cotton from acid baths, or mordanted cotton.



Night Blue is similarly obtained from *p*-tolyl-α-naphthylamine, and has similar dyeing properties.

Hydroxy Compounds—Aurine Series

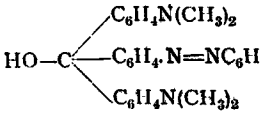
Aurine, rosolic acid, has already been referred to; it is used for colouring varnishes.



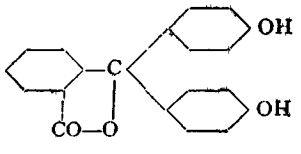
Chrome Violet, aurine tricarboxylic acid, is obtained from formaldehyde and salicylic acid; used for printing chrome mordanted cotton.

A number of mordant dyes of this series have been prepared recently; see English Patents, 15,204, 1907 (Geigy); 14,311, 1909; 14,312, 1909; 368, 1910; 1,411, 1910; 6,364, 1910 (Bayer); 12,130, 1910; 17,087, 1910 (M.L.B.).

We may finally note the azotriphenylmethane dyes, one of which, **Alizarin Yellow F.S.**, has already been referred to under azo dyes. They are obtained from triphenylmethane dyes containing free amino groups by diazotising and coupling with components and oxidising. For example—



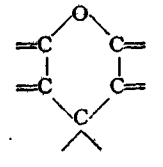
Azo Green is obtained from diazotised *m*-aminotetramethyldiaminotriphenylmethane and salicylic acid; dyes chromed wool.

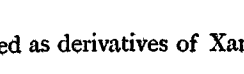
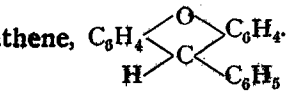


Phenolphthalein, the lactone of dioxytriphenylcarbinolcarboxylic acid, obtained from phenol and phthalic anhydride, may be classed in the aurine series, though its production is analogous to that of the phthaleins (*q.v.*); it is employed as an indicator in volumetric analysis.

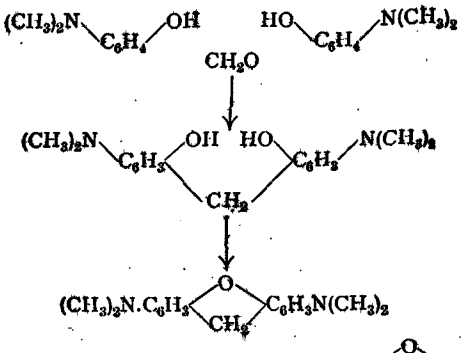
5. PYRONE DYES

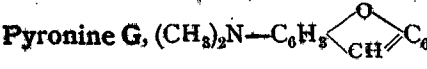
The dyes of this class are closely allied to the di- and tri-phenylmethane dyes, and are sometimes classed with them. It is more convenient, however, to treat them as a separate group and to regard them as pyrone or xanthene derivatives. They all contain the pyrone ring—



and may be regarded as derivatives of Xanthene,  , or of **Meso-Phenylxanthene**,  .

The Pyronines are obtained by condensing formaldehyde with dialkyl-*m*-aminophenols, thus—

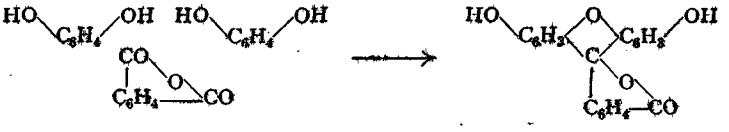


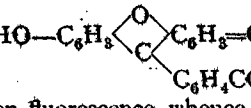
which on oxidation gives **Pyronine G**,  .

Pyronine B is the corresponding product from diethyl-*m*-aminophenol. These dye cotton, wool, and silk red, but are not very fast.

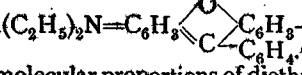
The next group to be considered are **Fluorescein** and its derivatives, the **Eosines**, etc.

Fluorescein is obtained by the reaction of phthalic anhydride on resorcin thus—

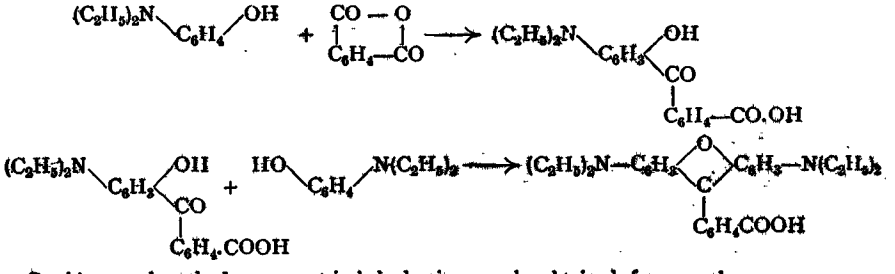


It may also be formulated  . Its alkali salts are soluble in water with a beautiful green fluorescence, whence the name. They dye silk and wool yellow. **Eosine**, tetrabromfluorescein, is obtained by brominating fluorescein. **Erythrosine**, tetraiodofluorescein, is obtained by iodising. **Erythrene** and **Spirit Eosine** are methyl and ethyl ethers of eosine. **Phloxine**, tetrabrom-tetrachlorfluorescein, is obtained by brominating the tetrachlorfluorescein from tetrachlorphthalic acid and resorcin. **Phloxine P** is the tetrabromdichlorfluorescein obtained by brominating the dichlorfluorescein from dichlorphthalic acid and resorcin. **Rose Bengal** and **Rose Bengal 3B** are the corresponding tetraiododichlor- and tetraiodotetrachlorfluorescein. These dye animal fibres yellowish red to bluish red shades; not very fast.

Fluorescein, as formulated above, is a dioxy-mesophenylxanthenecarboxylic acid or its lactone; the next group to be considered, the **Rhodamines**, are amino derivatives of mesophenylxanthene carboxylic acid.

Rhodamine B,  , can be obtained either by condensing two molecular proportions of diethyl-*m*-aminophenol with phthalic

anhydride, or by condensing equimolecular proportions of diethyl-*m*-aminophenol and phthalic anhydride to form diethyl-*p*-amino-*o*-oxybenzoylbenzoic acid, which is then condensed with a further molecular proportion of diethyl-*m*-aminophenol.



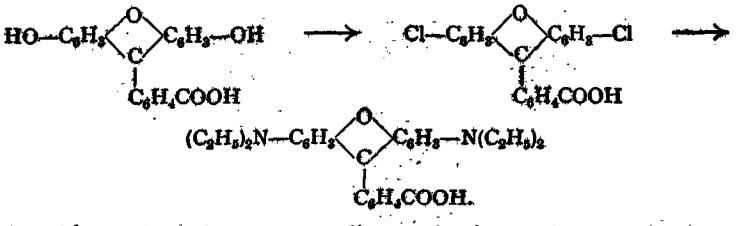
By this second method unsymmetrical rhodamines can be obtained, for example :—

Rhodine 2G from dimethylaminooxybenzoylbenzoic acid and ethyl-*m*-aminophenol, the carboxylic group of the dye being finally converted into its ethyl ester.

Rhodamine 12GM, from dimethylaminooxybenzoylbenzoic acid and resorcinmethyl ester, and esterification of the product.

Irisamine G, from dimethylaminooxybenzoylbenzoic acid and *m*-amino-*p*-cresol, the product being esterified.

Rhodamine B can also be obtained by converting fluorescein into its chloride by PCl_5, and treating the chloride with diethylamine :—



By applying this method the corresponding arylaminoxanthene derivatives can be produced, the sulphonic acids of which are acid wool dyes (whereas the Rhodamines described above are basic dyes, dyeing tannined cotton, wool, or silk various shades of red).

Examples of such acid dyes are :—

Fast Acid Violet B (Violamine B), $C_6H_5N{=}C_6H_3\langle{}^{O}_{C_6H_4COONa}\rangle C_6H_3{-}NH.C_6H_4SO_3Na$, obtained by sulphonating the product of reaction of aniline on fluorescein chloride.

Fast Acid Violet A2R (Violamine R), and **Violamine G**, are the corresponding sulphonic acids obtained by sulphonation of the products from *o*-toluidine and *p*-phenetidine respectively.

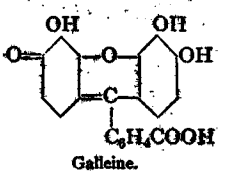
The above derivatives of phthalic acid are known as **Phthaleins**; succinic anhydride gives similar products known as **Succineins**. For example :—

Rhodamine S, $Cl(CH_3)_2N{=}C_6H_3\langle{}^{O}_{C_2H_4COOH}\rangle C_6H_3N(CH_3)_2$.

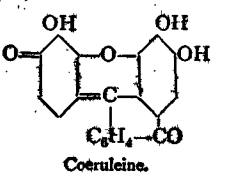
Finally, mention should be made of two phthaleins of somewhat different properties, viz. :—

Galleine from gallic acid or pyrogallol and phthalic anhydride, a violet mordant

dye, and **Caeruleine**, an anthracene derivative, obtained by treating galleine with concentrated sulphuric acid; a green mordant dye:—



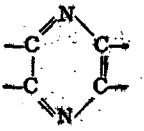
Galleine.

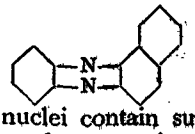


Coeruleine.

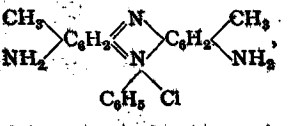
6. AZINE DYES

The azines are characterised by containing the azine (pyrazine, paradiazine) ring:—



The azine dyes of the anthracene series (indanthrene, etc.) have already been described. We shall consider here those azines which contain other aromatic nuclei. The simple azines, like diphenazine, , or naphthophenazine,  , like the simple azo compounds, are not dyes. But when the nuclei contain suitable substituents ("auxochromes"), such as NH_2 or OH, the products are in general dyes. It is now usual to formulate the azine dyes as possessing an ortho-quinonoid structure, and this practice will be followed in the succeeding pages.

In some cases, *e.g.*, the safranines, alkyl or aryl groups are attached to one of the two nitrogen atoms, which is then regarded as quinquevalent, the dyes being then referred to as azonium compounds,—*e.g.*, **Safranine T**—



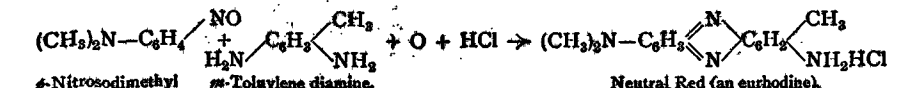
i.e., meso-phenyldiaminoditolylazonium chloride, mixed with the corresponding meso-tolyl body.

The principal group of azines to be considered are the **Eurhodines**, the **Rosindulines** and **Isorosindulines**, the **Safranines**, and the **Indulines**.

The **Eurhodines** are aminodiphenazines, the **Rosindulines** and **Isorosindulines** are naphthophenazine compounds, the **Safranines** are, as previously stated, meso-alkyl- or -aryl-diaminoazines, while the **Indulines** are meso-alkyl- or -aryl- tri- and -tetraaminoazines.

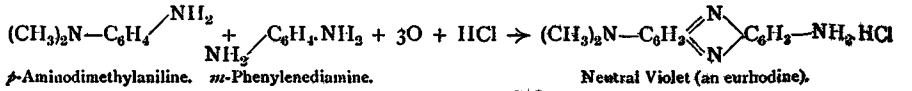
The following general methods for the production of azines should be noted:—

1. **Condensation and Oxidation of a *p*-nitroso derivative of an amine with a second amine.** For example:—

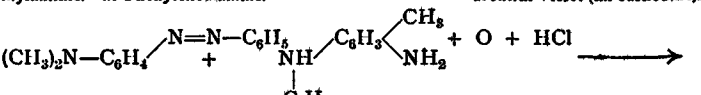


p-Nitrosodimethyl aniline. *m*-Tolylene diamine. Neutral Red (an eurhodine).

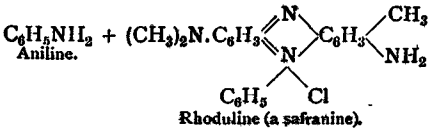
Instead of a *p*-nitroso compound, a *p*-diamine or a *p*-aminoazo compound may be used; for example:—



p-Aminodimethylaniline. *m*-Phenylenediamine. Neutral Violet (an eurhodine).



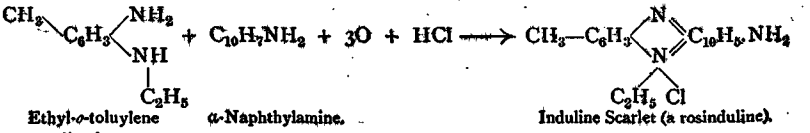
p-Phenylazodimethyl aniline. Phenyl-*m*-toluylene diamine.



Aniline. Rhoduline (a safranine).

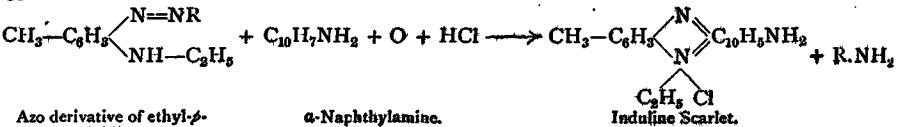
In the latter reaction it will be noted that the azo compound splits up and an amine forms as a bye-product.

2. **Both the azine nitrogen atoms may be obtained from an *o*-diamine or *o*-aminoazo compound**, *e.g.*:—



Ethyl-*o*-toluylene diamine. α-Naphthylamine. Induline Scarlet (a rosinduline).

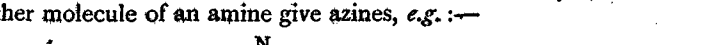
or



Azo derivative of ethyl-*p*-toluidine. α-Naphthylamine. Induline Scarlet.

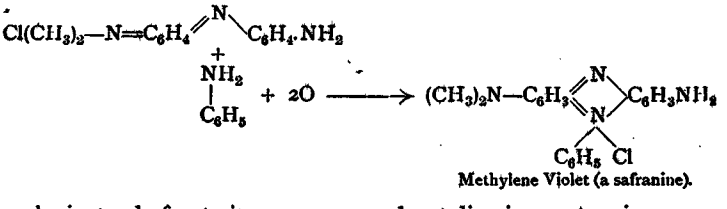
3. **The most important method is that in which three components are used**; this method is largely employed for obtaining Safranines.

Obviously this method is capable of yielding a great variety of products. The process may be carried out either in one step or two. If, for example, a *p*-nitroso compound of an amine is condensed with another amine, an intermediate product, an indamine, is formed, thus:—



p-Nitrosodimethylaniline. Aniline. Indamine.

The indamines are too unstable to be used for dyes, but on oxidation with another molecule of an amine give azines, *e.g.*:—

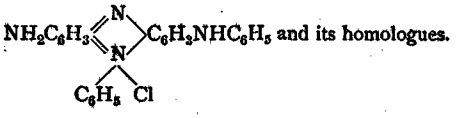


Methylene Violet (a safranine).

Obviously, instead of a *p*-nitroso compound a *p*-diamine or *p*-aminoazo compound may be used.

The three components may be directly condensed and oxidised to the azine without isolation of an intermediate indamine. This was the method by which

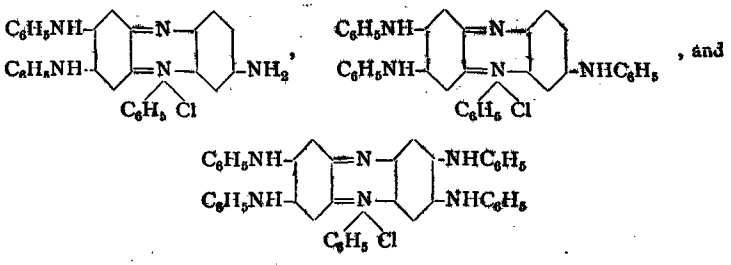
the first synthetic dye, **Mauveine**, was obtained by Perkin in 1856. Mauveine is a mixture of Safranines obtained by oxidising an impure aniline containing toluidine. It consists of—



Safranine T, previously referred to (p. 473), is obtained by this method from *p*-toluylene-diamine, analine, and *o*-toluidine, or *p*-toluidine and *o*-toluidine (two molecules.)

Similarly, **Phenosafranine**, mesophenyl-diaminophenazonium chloride, is obtained from *p*-phenylenediamine and two molecular proportions of aniline.

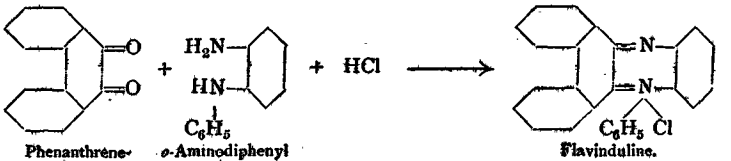
The indulines are produced by a similar method; **Induline** itself contains mesophenyl-dianilinoaminodiphenazonium chloride, and mesophenyl- tri- and -tetra-anilinophenazonium chloride:—



and is prepared by heating aminoazobenzene with aniline and aniline hydrochloride. Here arylamino groups are introduced into the molecule by means of the excess of aniline.

Nigrosine is similar in composition, and is prepared by heating aniline and its hydrochloride with nitrobenzene and a metal. These two dyes are principally used in the production of varnishes and inks (see p. 491).

4. **Another method which is a direct condensation without oxidation, viz., condensation of an *o*-diamine with an *o*-quinone,** is illustrated by the preparation of **Flavinduline**:—



Phenanthrene-quinone. *o*-Aminodiphenyl amine. Flavinduline.

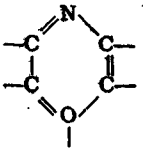
A large number of other azines are known, but the above are sufficiently typical and illustrate the general methods.

Those azines which contain only amino groups are in general basic dyes, dyeing tannin-mordanted cotton or silk usually red, violet, or blue shades. When sulphonic acid groups are present, *i.e.*, when the dyes are derived from sulphonated parent materials, or are sulphonated after their production, the products are acid wool dyes; practically the only recent developments in the azine series are in the production of acid wool dyes of the Safranine type.

We may note finally that some azo dyes have been prepared by diazotising azine dyes containing amino groups and coupling with β-naphthol, etc.; **Indoin Blue** (diazotised Safranine T + β-naphthol) is an example.

7. OXAZINE DYES

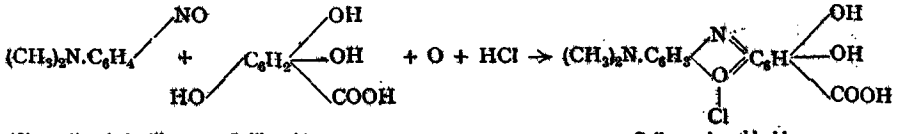
The oxazine dyes are analogous to the azines, but contain, instead of the azine ring, the oxazine ring :—



The oxazines are usually formulated as ortho-quinonoid compounds. It will be seen from the examples given below that the general methods of preparation are analogous to those employed in the production of the azines.

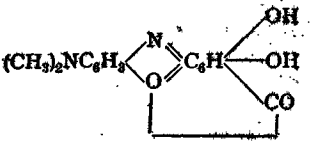
The most important group of oxazines is the **Gallocyanines**, which are obtained from gallic acid and its derivatives, and are employed for producing blue shades by printing on cotton or wool with chrome mordants.

Gallocyanine itself is prepared from nitrosodimethylaniline and gallic acid :—



Nitrosodimethylaniline. Gallic acid. Gallocyanine chloride.

The free base may be formulated as the anhydride :—

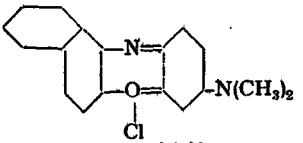


By using derivatives of gallic acid other gallocyanines are produced, *e.g.*, **Prune**, from nitrosodimethylaniline and methylgallate; **Gallamine Blue**, from nitrosodimethylaniline and gallamide; **Celestine Blue B**, from nitrosodiethylaniline and gallamide. In these processes the *p*-aminoazo compounds can be used instead of the *p*-nitroso bodies (*cf.* the corresponding processes for preparing azines).

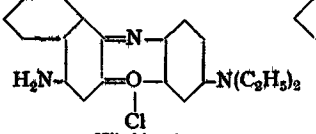
Reduction converts the gallocyanines into their leuco derivatives (**1900 Blue**, **Modern Violet**, etc.), which for some purposes are preferable to the parent dyes. The action of bisulphites also give products which are probably modified leuco derivatives. Gallocyanines can be condensed with aromatic amines or phenols; for example, **Delphine Blue** is prepared by condensing gallocyanine with aniline and sulphonating the product, while **Phenocyanine VS** is obtained from diethylgallocyanine and resorcin. By heating ordinary gallocyanine in solution or suspension in an acid, neutral or alkaline medium, CO_2 splits off and a pyrogallol-gallocyanine is obtained (see English Patents, 20,802, 1906; 9,961, 1907; 1,334, 1908).

The other oxazine dyes need not be discussed at length. Examples are :—

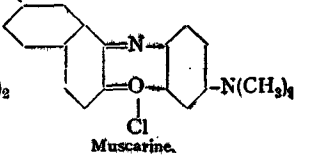
Meldola's Blue (New Blue), from nitrosodimethylaniline and β-naphthol; **Nile Blue A**, from nitrosodiethyl-*m*-aminophenol and α-naphthylamine; **Muscarine**, from nitrosodimethylaniline and 2 : 7-dioxynaphthalene.



Meldola's blue.



Nile blue A



Muscarine.

8. THIAZINE, THIAZOLE, AND SULPHIDE DYES

These three groups of dyes are conveniently considered together, as they are each characterised by containing sulphur, in a ring or otherwise.

The **Thiazines** contain the six-membered ring—

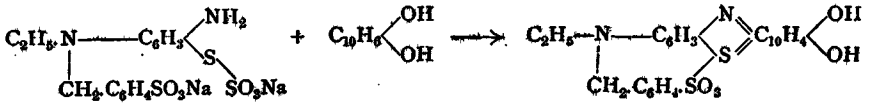
which may be compared with the azine and oxazine rings.

A typical thiazine is **Methylene Blue**, tetramethyldiaminodiphenazthionium chloride, $(CH_3)_2N.C_6H_3\langle{}^{N}_{S}\rangle C_6H_3N(CH_3)_2$, Cl. It is prepared by oxidising dimethyl-*p*-phenylenediamine together with sodium thiosulphate to give the thiosulphonic acid, $(CH_3)_2N.C_6H_3\langle{}^{NH_2}_{S.SO_3H}$, which is then oxidised with dimethylaniline to the indamine, $(CH_3)_2N{=}C_6H_3{=}N{-}C_6H_4{-}N(CH_3)_2$, O_3S, S, which, on further oxidation, gives first Leucomethylene Blue, $(CH_3)_2N.C_6H_3\langle{}^{NH}_{S}\rangle C_6H_3{-}N(CH_3)_2$, and then the dye.

Methylene blue is a basic dye, dyeing tannin-mordanted cotton. It has also therapeutic properties.

New Methylene Blue N, diethyldiaminotoluphenazthionium chloride, is obtained similarly from *p*-aminoethyl-*o*-toluidine, sodium thiosulphate, and ethyl-*o*-toluidine, and has similar properties.

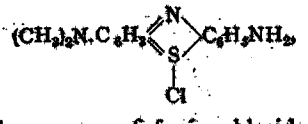
Brilliant Alizarin Blue, ethylbenzylaminophenodioxynaphthazthionium sulphonic acid anhydride, is obtained by oxidising *p*-aminoethylsulphobenzylaniline thiosulphonic acid and *β*-naphthohydroquinone:—



It dyes chromed wool, cotton, or silk.

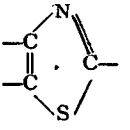
Another method of obtaining the thiazine ring consists of the use of sulphuretted hydrogen and ferric chloride; for example:—

Gentianine, dimethyldiaminodiphenazthionium chloride,

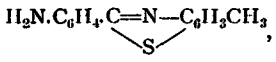


is obtained by oxidising by means of ferric chloride, *p*-phenylenediamine with dimethyl-*p*-phenylenediamine in presence of sulphuretted hydrogen.

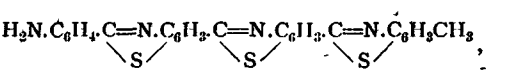
The **Thiazoles** contain the five-membered ring :—



The typical thiazole is **Primuline**, a yellow direct cotton dye; it is obtained by heating *p*-toluidine with sulphur, whereby dehydrothiotoluidine,



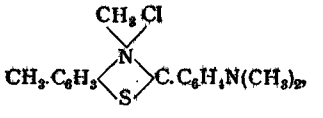
is first formed; this, on further heating with sulphur, condenses to the primuline base :—



which is sulphonated to give Primuline.

As previously described, Primuline can be diazotised and combined with azo dye components, and it is used thus for producing azo dyes on the fibre (see **Developing Dyes**, p. 450).

Methylation of dehydrothiotoluidine gives **Thioflavine T**,



which dyes tannin-mordanted cotton or silk greenish yellow.

The Sulphide Dyes (p. 545) form a very large and important group. They are characterised in general by the property of dissolving in sodium sulphide solutions and dyeing cotton from such a bath. Some, however, are insoluble in sodium sulphide, but dissolve in alkali hydrosulphite and thus behave as vat dyes. The method of preparation is very simple, consisting in melting the parent substance with sulphur or more usually with sulphur and sodium sulphide. The parent substances used are very diverse. The first sulphide dyes were prepared from natural organic bodies, such as sawdust, bran, woodpulp, etc., and the product, **Cachou de Laval**, dyed cotton brown shades. The first sulphur dye from a synthetic organic compound was **Vidal Black** from *p*-aminophenol. A large number of sulphide dyes have been prepared from diphenylamine derivatives, *e.g.*, **Immedial Black V**, from dinitrooxydiphenylamine, **Immedial Sky Blue**, from diethyl-*p*-amino-*p'*-oxy-diphenylamine.

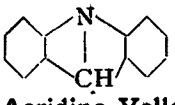
Cassella & Co. form indophenolic bodies by condensing *p*-nitrosophenol with carbazole or its N-alkyl, etc., derivatives; and then sulphurise. **Hydroïn Blue R** and **G** (see English Patents, 2,918, 1909; 9,689, 1909; 14,143, 1909; 18,822, 1909; 22,138, 1910) are vat dyes of this type.

The sulphur dyes derived from anthraquinone have already been referred to (see **Anthracene Dyes**, p. 458).

Although so many sulphur dyes have been prepared, their constitution is not known with certainty. Probably many of them, for example, Immedial Sky Blue, contain a thiazine ring, and also contain a thio or dithio group (R.S.H. or R.S.S.R.).

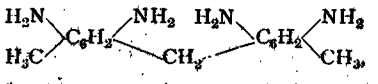
9. ACRIDINE DYES

This is a small group of basic dyes, which contain the acridine nucleus,

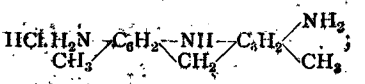


. A typical method of preparation may be illustrated by the case of **Acridine Yellow**, diaminodimethylacridine; condensation of formaldehyde with

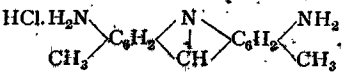
m-toluylenediamine gives tetraminoditolylmethane



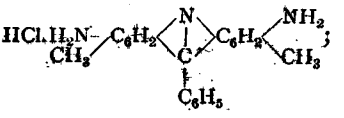
from which, on heating with acids, ammonia splits off, giving a hydroacridine derivative:



this on oxidation, say, with ferric chloride, gives the dye,

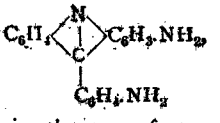


A similar condensation, using benzaldehyde and *m*-toluylenediamine, gives **Benzoflavine**, diaminodimethyl-meso-phenylacridine,

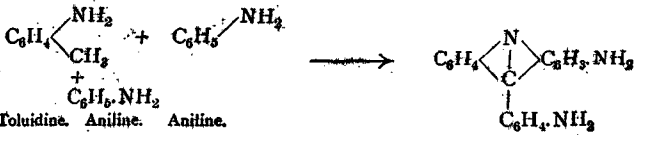


dyes yellow shades.

Another yellow acridine dye, which is used for dying leather, is **Phosphine**, a diaminophenylacridine,



first obtained as a by-product in the manufacture of Rosaniline. Its formation may be represented thus—



10. MINOR GROUPS OF DYES

A brief description will be given here of a number of small groups of dyes:—

(*a*) **Nitro Dyes.**—Some simple nitro compounds possess dyeing properties. Examples are: **Picric acid** (trinitrophenol), **Martius yellow** (dinitro-α-naphthol), **Naphthol yellow S** and **RS** (dinitronaphthol sulphonic acids), **Aurantia** (hexanitrodiphenylamine); all are acid wool dyes.

Picric acid is still used to some extent for silk and leather.

(*b*) **Nitroso-Phenol** or **Quinoneoxime Dyes.**—These are practically obsolete dyes; examples are **Fast Green O** (dinitrosoresorcin or benzoquinonedioxime), **Gambine R** and **Y** (nitrosonaphthols or naphthoquinoneoximes), **Dioxine** (nitrosodioxynaphthalene or oxynaphthoquinoneoxime); these are mordant dyes.

(*c*) **Quinoline Dyes.**—These are chiefly of interest because of the use of some of them in photography (see **Photographic Chemicals**, p. 655).

Cyanine, obtained by the action of amyl iodide on a mixture of quinoline and lepidine, and **Quinoline Red**, from benzotrichloride, quinoline, and isoquinoline, are examples of these.

Quinoline Yellow, quinophthalone, is obtained from quinaldine and phthalic anhydride; sulphonation of this product gives a soluble wool dye.

(*d*) **Oxyketone Dyes** (other than anthracene derivatives).—A few mordant dyes of this type may be noted. **Alizarin Yellow A**, trioxybenzophenone, from benzoic acid and pyrogallol; **Alizarin Yellow C**, trioxyacetophenone, from acetic acid and pyrogallol; **Galloflavine**, obtained by oxidising gallic acid; and **Alizarin Black S** or **Naphthazarine S**, the bisulphite compound of naphthazarine,

, obtained from dinitronaphthalene by Zn + conc. H_2SO_4, or S + SO_3.

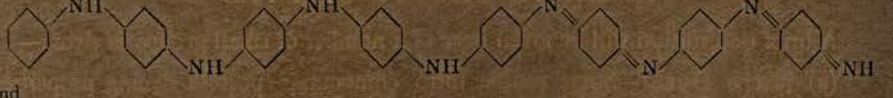
(*e*) **Indamines and Indophenols.**—These are compounds of the type $NH_2C_6H_4—N=C_6H_4=NH$ and $NH_2C_6H_4—N=C_6H_4=O$, respectively. They are

Indamine. Indophenol.

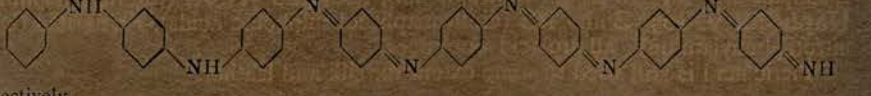
too unstable to be used as dyes; the production of indamines as intermediate products in the manufacture of azine and thiazine dyes has already been referred to (*q.v.*). On reduction they yield diphenylamine derivatives, and hence they are of importance as the parent materials for the manufacture of sulphur dyes.

(*f*) **Aniline Black.**—This old and still highly important dye should be more properly discussed under dyeing, since it is practically always formed on the fibre, by impregnating the material with aniline salts and oxidising by means of chlorates, etc. Many variations on the process have been suggested, chiefly with a view of obtaining a black which will not turn green. One of the most recent processes is that of Green (English Patent, 16,189, 1907), according to which a small quantity of *p*-phenylenediamine, *p*-aminophenol, or the like, is added to the aniline, and the oxidation is effected by air, the *p* phenylenediamine, etc., being supposed to act catalytically.

The constitution of aniline black has been the subject of many researches. It has the empirical formula $(C_6H_5N)_x$. According to Green and Woodhead (*Journ. Chemical Society*, 1910, p. 2388), a series of quinonoid bodies containing eight nuclei can be obtained by oxidation of aniline, viz., proto-emeraldine, emeraldine, nigraniline, and pernigraniline, the first and last of these being unstable bodies; aniline blacks prepared in substance consist of a mixture of emeraldine, nigraniline, and higher condensation products, while the blacks produced on the fibre consist largely of higher condensation products. **Emeraldine** and **nigraniline** are formulated as—

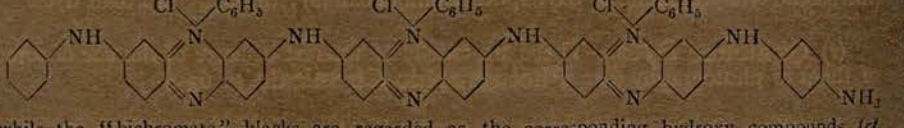


and



respectively.

In subsequent publications (*Journ. Soc. Dyers*, 1913, pp. 105 *et seq.*, 338 *et seq.*), Green develops the view that his blacks are **azonium** compounds, obtained by conjoint oxidation of products of the emeraldine series with a further amount of aniline; the "aged" and "chlorate" blacks are formulated as—



while the "bichromate" blacks are regarded as the corresponding hydroxy compounds (*cf.* English Patent, 19,124, 1912).

For **Dyeing Processes** with Aniline Black (see pp. 544, 556, 557).

SECTION XIV

The Industry of Natural Dye-Stuffs

THE INDUSTRY OF NATURAL DYE-STUFFS

By G. Martin, Ph.D., M.Sc.

LITERATURE

H. Rupe.—"Die Chemie der naturlichen Farbstoffe." 2 vols., 1900 and 1909.
R. Lowenthal.—"Handbuch der Farberei." 1900.
Zerr and Rübencamp.—"Treatise on Colour Manufacture." 1908.

The natural colouring matters of animal and vegetable origin have been used for dyeing for hundreds, and in some cases for thousands, of years. Since the manufacture of the artificial colouring matters from coal-tar their use has enormously decreased. A few, however, still possess some importance, viz., indigo and logwood. Artificial indigo, however, is now being manufactured in large quantities, and no doubt in course of time the use of the natural colouring matters will entirely die out, being replaced by superior and cheaper synthetic products.

Statistics.—The following figures show the value of the natural dye-stuffs imported into the United Kingdom:—

	1906.	1910.	Value.
	Cwt.	Cwt.	£
Cochineal	2,270	1,269	7,321
Cutch	5,217	3,202	86,803
Natural indigo	7,641	3,350	43,054
Logwood	359,820	217,340	42,000
Other dye woods	70,360	104,360	38,755

Dye wood extracts were valued in 1908 at £176,318; in 1910 at £156,359.

The United States imports were:—

	1906.	1910.	Value in 1910.
Cochineal	111,000 lbs.	151,000 lbs.	$41,000
Cutch	...	28,000 ,,	1,278
Indigo (natural)	193,000 lbs.	125,000 ,,	66,000
Annatto	...	619,372 ,,	40,000
Turmeric	...	...	28,000
Dye woods in a crude state—			
Fustic	...	5,800 tons	83,000
Logwood	37,000 tons	32,000 ,,	368,000
All other	...	923 ,,	33,000
Extracts—			
Logwood and other dyewoods	3,390,000 lbs.	3,270,000 lbs.	198,000
Persian berries	...	83,000 ,,	8,000
Chlorophyll	...	4,000 ,,	3,000

Black and Blue Colouring Matters

Indigo is treated under **Coal-tar Colours**, p. 459.

Logwood* (Campeachy wood, German, *Blauholz*, wood of *Hæmatoxylon campechianum* of Central America) contains a colouring matter termed **hæmo-**

* See also pp. 490, 551, 552.

toxylin, $C_{16}H_{14}O_6 + 3H_2O$ (yellow prisms, p. 490), which when oxidised is converted into the real colouring matter, hæmatein, $C_{16}H_{12}O_6$. This is soluble in alkalis giving a deep blue colour, and violet precipitates with aluminium salts, blue with copper, and black with iron and chromium. For dyeing purposes the wood in the form of sawdust or chips was formerly used, but now extracts are usually employed.

1. In the **American Method of extraction** the wood is extracted five times for fifteen minutes in autoclaves at 1-5 atmospheres pressure. The largest yield is thus obtained, but it contains impurities such as resin, tannic acid, sugar, etc., which influence the dyeing unfavourably.

2. In the **French Method** the extraction is made by simply boiling the wood under ordinary pressure, yielding a good and copious extract.

3. In the **Diffusion Method** the wood is extracted similar to the extraction of beets in the sugar industry. Yield small but of best quality, and therefore dear.

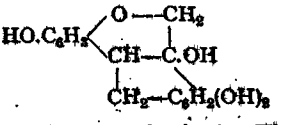
The extract is settled in large tanks, filtered through cloth, and concentrated by evaporation. Up to 10° Bé. the extracts are fluid; 30°-40° Bé. yield solid extracts. Logwood is exclusively used for *black* dyeing of silk, using an iron salt and some yellow colouring matter to kill the blue tone. Also used for dyeing and printing black and grey shades on calico and wool, and for shading with a blue tone other colouring matters. Except for black silk its use is being displaced by artificial colouring matters. For **Dyeing Processes**, see pp. 551, 552.

Tests.—Logwood chips may be adulterated with syrup extracts containing tannin (*e.g.*, chestnut extract) or "foots" or with excess of moisture. (1) A microscopic examination usually reveals nature of contamination. (2) Estimate the moisture (drying weighed quantity chips at 100° C.). If it contains more than 14 per cent. (usual quantity) it is adulterated and may take up 40 per cent. moisture. (3) The only reliable test is an actual dyeing test with white wool, made with definite weights of wood, thoroughly extracted, and definite weights of mordants.

Red Colouring Matters

Madder (German, *Krapp*).—Now displaced by artificial alizarin (p. 451), which see.

Redwood, Brazil Wood (*Rotholz, Bois rouge*).—Many different varieties are known (*Family* Leguminosæ, genus Cæsalpinia, found in East Indies, Central and South America, etc.). It contains the colourless base **brasilin**, $C_{16}H_{14}O_5$, which when carefully oxidised furnishes the red colouring matter **brasilein**, $C_{16}H_{12}O_5$. The constitution of brasilin is believed to be as shown—



but the substance has not as yet been synthesised. The colour is not very fast, and its use is dyeing cotton, and printing to produce mixed shades; also for wool and oils.

Santalwood (*Sandelholz*, East Indies) contains 16 per cent. of **santalin**, $C_{15}H_{14}O_5$; the extract is used for colouring confectionery, liqueurs, tinctures, etc.

Archil (*Orseille, Oricello, Orchilla*) is obtained from the algal genera *Roccella, Variolaria*, and *Lecanora*, by extracting the plants with water and warming the liquor with ammonia, when the archil is precipitated as a paste. The actual colouring principle is **orcin**, $C_6H_3(CH_3)(OH)_2$, which in the presence of air and ammonia oxidises to the violet dye orcein, $C_{28}H_{24}N_2O_7$.

Litmus (*Lachmus, Tournesol*) is likewise obtained from certain algæ (species of *Roccella* and *Lecanora*) in the East Indies, tropical America, and Canary

Islands, Scandinavian and Mediterranean coasts. The algæ are dried, ground, mixed with ammonium carbonate, potash, and lime, allowed to stand three weeks, when the material ferments and produces a blue colour. More ammonia and chalk are added, and the mass pressed into cubes and dried. Contains several colouring matters (azolitmin, litmum, etc.), which in free state are red, but with alkali form **blue** salts (hence acids turn litmus red, alkalis blue). Used as an indicator in chemistry, also for colouring liqueurs, confectionery, preserved fruit, etc. etc.

Carotine is the yellow-red colouring matter of carrots, and is used for colouring butter and cheese.

Alkanet, $C_{15}H_{14}O_4$, is obtained by extracting the root of the *Alcanna tinctoria*, and is used for colouring oils, salves, hair-oils, etc., and other cosmetic articles, since it is soluble in such media and fast.

Carmine (Cochineal) is a colouring matter contained in the females of the insect *Coccus cacti* (Mexico and Central America). The females are collected shortly before the laying season, killed by steam, dried, and sold as colouring matter under the name **Cochineal**. The colouring matter is **carmine**, which is obtained by extracting the insects with boiling water, precipitating with alum, washing and drying; it is stated to be an **aluminium calcium protein** compound of the carmine colouring matter. The cochineal insects contain 10 per cent. carminic acid, $C_{22}H_{22}O_{13}$, which is hydrolysed by dilute sulphuric acid into sugar and **carmine red**, $C_{11}H_{12}O_7$. **Carmine** is used for making face powders, colouring sweets, puddings, etc., being non-poisonous (see also p. 552).

Lac-dye, a product similar to cochineal in origin and use, is obtained from **gum-lac**, an exudation product formed by certain tree-boring insects, by extracting with sodium carbonate solution. The residue left behind forms the ordinary **shellac** (see pp. 348, 552).

The **Purple** of the ancients was obtained from a snail inhabiting the sea-coasts of the Mediterranean (see p. 420).

Yellow, Brown, and Green Colouring Matters

Fustic (Brazil wood, yellow wood, *Gelbholz*), from *Morus* (Maclura) *tinctoria*, contains **Morin**, $C_{15}H_{10}O_7$, and Maclurin, $C_{13}H_{10}O_6$ (a non-colouring material). **Morin** gives a yellow lake with aluminium salts, used for colouring wool yellow. Not very fast to light (see p. 552).

Quercitron, the yellow powdered bark of the oak *Quercus tinctoria* of North America, contains quercitrin, $C_{21}H_{22}O_{12} + 2H_2O$, which, on boiling with dilute acids, hydrolyses into isodulcite, $C_6H_{14}O_6$, and the yellow dye **Quercitin** or **Flavin**, $C_{15}H_{10}O_7$. Both quercitrin and quercitin form yellow lakes with aluminium and tin salts, and are consequently used for wool dyeing and printing, and largely for shading other colours (see p. 552).

Persian Berries, Yellow Berries (*Kreuzbeeren*) contain **xanthorhamnin**, a glucoside which dilute mineral acids hydrolyse into **isodulcite** and the yellow dye **rhamnetin**, $C_{10}H_{12}O_7$; the latter substance yields, when fused with potash, proto-catechuic acid, $C_6H_3(OH)_2.CO_2H$. Yields yellow lakes with chromium, tin, and aluminium salts, fast to soap and chlorine, but only moderately fast to light. An extract is used as painters' colour and for staining paper and leather yellow (see p. 552).

Annatto (Orleans, Anatto, *Terra orellana*), obtained from the fleshy covering of the ruccu tree (*Bixa orellana*) of Central America, contains a yellow colouring matter, **bixen**, $C_{28}H_{34}O_5$, and the extract is used for colouring butter, cheese,

margarine (see pp. 75, 87, 546), etc. When annatto has been adulterated with mineral bodies, more than 10 per cent. of ash will be found.

Turmeric (Curcuma, *Gelbwurzel*).—The powdered root of the *Curcuma longa* and *C. rotunda*, contains a yellow colouring matter, **curcumine**, which can be extracted with ether, alcohol, and alkalis. Although not fast to soap or light, the substance is a useful colouring agent for wool, silk, oil, butter, and cheese (see pp. 75, 87, 546).

Woad (Luteolin, Wau, *Gelbkraut*), from *Reseda, R. luteola*, contains **luteolin**, $C_{15}H_{10}O_6$, and dyes silk a fast yellow (with aluminium salts as mordant).

Indian Yellow, Purree (*Purrea arabica*, Piuri) is prepared at Monghyr (Bengal) from the urine of cows, fed on leaves of the mango tree. The colouring principle is the magnesium and calcium salt of euxanthic acid, $C_{19}H_{16}O_{11}Mg + 5H_2O$. Used as a permanent water and oil colour. If adulterated with chrome yellow it gives a black coloration with H_2S. If yellow aniline lakes be present the solution remains yellow when concentrated HCl is added (if pure a colourless solution should result, depositing white flakes of euxanthic acid).

Cutch (Cachou, Catechu, Japan Earth) is the brown amorphous extract obtained by boiling with water the wood of various kinds of **Acacia** in India and the East Indies. It contains **catechin** and **catechu-tannic acid**; the latter is used for tanning purposes, and being soluble in cold water may be separated from the catechin by washing cutch with cold water; crude **catechin** remains, which, being recrystallised from hot water, is obtained as fine, white, silky needles, M.P. 217° C., and of formula $C_{21}H_{20}O_9$. Cutch is used in cotton dyeing and printing, producing brown, black, grey, and olive shades, very permanent and fast to light, soap, acids, and bleaching powder. Also used for silk and wood stains (see p. 549).

Dragon's Blood is a deep or brown-red resin obtained from species of **Calamus** (India, Sumatra, Moluccas) and used for colouring spirit varnishes, toilet articles, etc., a deep red (see p. 348).

Gamboge (*Gumigutt, Gutti*) is the resin of *Garcinia Morella* (East Indies, Ceylon); forms a yellow water colour, sometimes used for colouring spirit and other varnishes; poisonous; used in pharmacy (see p. 348).

Saffron, Crocus (*Safran*), from dried and powdered flowers of saffron plant, *Crocus sativus* (Orient); used for colouring confectionery (see pp. 75, 87, 546).

A **green** colouring matter is **Chlorophyll**, found in green leaves and stalks of plants, obtained by extracting grass, etc., with alcohol (or with dilute caustic potash and precipitating by mineral acids). Is fugitive in light, but is used for colouring confectionery, liqueurs, and toilet articles.

SECTION XV

The Ink Industry

THE INK INDUSTRY

By G. Martin, Ph.D., M.Sc.

LITERATURE

C. Ainsworth Mitchell and T. C. Hepworth.—"Inks, their Composition and Manufacture." 1904. (Gives English Patents to 1904.)
Sigmund Lehner.—"Ink Manufacture." 1902.
Schluttig and Neumann.—"Untersuchungen Eisengallustinten." 1909.
A. Buchwald.—"Bleistifte, Farbstifte." 1904.

Black Writing Inks

Gallotannic Inks.—The ordinary writing inks consist, principally, of the iron salts of gallotannic and gallic acid substances contained in vegetable tannins. Gallotannic acid occurs in gall tannin and has the formula:*—

$$C_6H_2(OH)_3—CO—O—C_6H_2(OH)_2COOH.$$

When hydrolysed by hot acids, or by fermentation, it breaks down into **gallic acid**, $C_6H_2(OH)_3COOH$. Gallotannic acid yields blue or black compounds with iron salts. Gallic acid, however, produces no coloration with ferrous salts, but the solution on standing gradually oxidises to the ferric state, becomes black, and deposits an insoluble black precipitate. In consequence of this property the ordinary writing inks of commerce are ferrous (unoxidised) inks with gallic or gallotannic acid, and being usually of a very pale colour, have added to them a provisional colouring matter, such as indigo sulphonic acid, soluble blue, etc. The ink on penetrating into the fibres of the paper oxidises after some days into the black ferric compound, and so is not easily removed by washing. The presence of indigo increases the permanency of the ink, and makes it more resistant to the action of bleaching agents.

A good ink of this nature consists of an extract of 42 parts Aleppo galls in 120 parts of water, mixed with 1·2 parts of indigo solution (indigo sulphonic acid), or some other blue aniline dye, such as aniline blue, fast blue, etc. To this are added 5·5 parts of ferrous sulphate and 2 parts of metallic iron dissolved in crude acetic acid (pyroligneous liquor). A certain amount of antiseptic—say 2 lbs. phenol to 1,000 gals. of ink—is usually added to prevent the ink from becoming mouldy.

State of Massachusetts official ink contains: Dry gallotannic acid, 23·4; gallic acid crystals, 7·7; ferrous sulphate, 30; gum arabic, 25; dilute hydrochloric acid, 25; phenol, 1; all dissolved in 1,000 parts of water.

Dieterich recommends the following ink: 60 g. tannin are dissolved in 540 c.c. of water; 40 g. of ferric chloride solution, containing 4 g. of iron, are mixed with 1 g. of sulphuric acid and 400 c.c. of water. The solutions are mixed, boiled ten to fifteen minutes, and then 30 g. of sugar and 10 g. of aniline water blue 3B are added. The ink flows easily from the pen with a deep blue colour, and dries blue-black; copies taken are blue at first but become black.

Gallic Acid Inks.—When gallotannic acid is hydrolysed by acid or allowed to ferment it breaks up into gallic acid, $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$. After the conversion of gallotannic acid into gallic acid twice as much ink is produced from a given amount of ferrous sulphate—a fact which has given rise to Gallic Acid Inks, which we will briefly describe:—

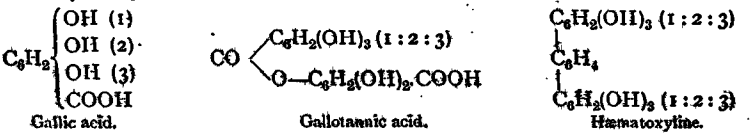
Ink from Fermented Gall Extract.—200 parts of powdered Chinese galls are kept moist (but not wet) at 20°-25° C. until mouldy (eight to ten days), when most of the gallotannic acid has fermented into gallic acid. The galls are thoroughly extracted with hot water, talc is added, the

* Recent research has shown that the tannins consist of several complex substances.

solution filtered, and made up to 1,000 parts by weight; then 100 parts of ferric chloride solution containing 10 per cent. of iron are added, and the ink left for two weeks in closed flasks, decanted, and a provisional colour added, which, for a **blue-black** ink, consists of 3 parts of phenol blue in 400 parts water + 1 part phenol; this is added to 600 parts of the ink solution, the whole kept for a week in a loosely-covered flask, and then decanted. A **black ink** is given by 10.5 parts aniline green + 9 parts ponceau red R + 1 part phenol blue 3F dissolved in water and added to the ink solution.

Ink from Hydrolysed Tannin Solution.—100 parts of tannin, 100 of water, 200 of ferric chloride solution (10 per cent. iron), and 10 parts of crude hydrochloric acid (sp. gr. 1.16), are heated for ten hours at 80°-90° C. (in order to hydrolyse the gallotannic acid into gallic acid), then diluted with 700 parts of hot water, heated to 80° C. for one hour, cooled, kept in a closed bottle for two weeks, filtered, and diluted to 1,000 parts. A provisional colour must be added, since the writing at first is barely susceptible, although it ultimately oxidises to deep black. The provisional colour may be the same as that in the preceding ink.

Chemical Nature of Tannin Inks.—Schluttig and Neumann showed that benzene derivatives containing three or more hydroxyl derivatives in juxtaposition yield permanent inks with iron compounds. For instance, hydroquinone, $C_6H_4(OH)_2$, does not yield an ink with iron salts, whilst gallic acid, gallotannic acid, and hæmotoxyline (the colouring principle of logwood), each of which contain three adjacent hydroxyls, all yield permanent inks with iron salts:—



Gallic acid. Gallotannic acid. Hæmatoxyline.

The precise nature of the iron compounds which occur in tannin inks is unknown; no doubt several individual bodies exist and contribute to the effect. The experiments of Pelouze, Wittstein, and Schiff point to the existence of the basic tannate $(C_{14}H_9O_9)_3Fe—Fe(C_{14}H_9O_9)_3$. Chemically, however, the whole subject is very obscure.

Tannin Materials for Inks.—Tannins of various kinds occur widely distributed in the vegetable kingdom, and consequently there exist a large number of vegetable products from which inks can be made. Among these may be mentioned: **Galls**, vegetable excrescences formed upon the branches, shoots, and leaves of trees by the puncture of the young tissues by the females of certain insects for the purpose of depositing eggs. Many varieties of galls occur, such as **Oak Apple Galls, Aleppo Galls** (Turkey or Levant Galls), **Chinese Galls, Japanese Galls, Acorn Galls**, etc. These contain from 40-70 per cent. of tannin, estimated as gallotannic acid.

Other ink-making materials are: **Chestnut Extract** (from the wood or bark of chestnut tree), **Sumach Divi-Divi, Myrobalans, Valonia, Oak Bark**, etc., all of which materials are rich enough in tannins to yield good inks. (See also under **Leather Manufacture**, p. 573).

Tannins may be divided into "**iron-blueing**" and "**iron-greening**" according to the colour of the precipitate they form with iron salts. Only the **iron-blueing** tannins are suitable for the manufacture of black ink. Oak-bark tannin, although an iron-greening tannin, contains a substance giving a blue precipitate with iron salts and consequently can be used for ink manufacture. Tannins suitable for leather (see **Leather Manufacture**), are often unsuitable for inks.

Statistics.—The amount of galls imported into Britain was 18,500 cwt. (value, £62,000) in 1906, and 15,600 cwt. (value, £37,000) in 1910. The amount of the other vegetable tannins is given under **Leather**.

Logwood Inks.—Logwood extract (see **Logwood, Natural Colouring Matters**) is often added to iron gall inks, improving its colour without injuring its permanency. A common recipe is 3 parts of galls, 1 of ferrous sulphate, 1 of logwood, in 50 parts of water, with gum arabic in proportion of 1 part to 40 of ink.

A copper logwood ink consists of logwood extract, 20 kilos. in 200 kilo. water, mixed with 10 kilos. of ammonium alum previously dissolved in 20 kilos. of boiling water, 0.2 kilo. sulphuric acid, 1.5 kilos. copper sulphate in 20 l. of water. A provisional colouring matter (indigo sulphonic acid, phenol blue, etc.) must be added. The copper destroys steel pens.

Dieterich's School Ink is a bichromate logwood ink, consisting of 200 parts of a 20 per cent. logwood extract solution diluted to 500 c.c. and heated to 96° C. Then a solution of 2 parts of potassium bichromate, 50 of chrome alum, and 10 of oxalic acid dissolved in 150 of water are added drop by drop, the mixture maintained at 90° for thirty minutes, and then diluted to 1,000 parts, 1 part of phenol added, and the whole allowed to stand two to three days, decanted, and is then ready for use.

Black Aniline Inks.—A black ink stylographic pen consists of a solution in water (1 part dye to 80 parts water) of the various brands of water-soluble nigrosines (the sodium salts of the sulphonated nigrosines, see **Dyes**, p. 475). Such solutions have no action on metallic pens, and dry well, but lack the permanency of a good iron gall ink. Induline blue (B) (p. 475) forms a similarly constituted **blue** ink.

Coloured Writing Inks

These are usually made from water-soluble aniline dyes such as the following, the proportions being 1 part dye to 50-80 parts of water.

For Red Inks.—Eosin, erythrosin, ponceau scarlet, or cotton scarlet.
For Green Inks.—Neptune green S.G., diamond green G.
For Blue Inks.—Indigo carmine, or soluble blue T.
A good blue ink (fast) is made by triturating 10 parts freshly precipitated Prussian blue, 1 part of oxalic acid, and adding water gradually.
Violet.—Acid violet 4B.L.
Yellow.—Fast yellow or tartrazin in water.

Gold Ink.—Gold leaf, mixed with honey, is ground fine, washed, dried, and suspended in gum-arabic (1) + 1 of soluble potash glass dissolved in 4 of water. Substitutes for gold are Dutch leaf or bronze powder. **Silver ink** = powdered silver (or Aluminium foil) rubbed up with gum or the preceding medium.

Essentials of a Good Writing Ink.—(1) The writing should be permanent. (2) The ink should flow readily from the pen. (3) It must penetrate deeply into the fibres of the paper without passing right through. (4) It must not become mouldy or thick in the ink pots. (5) It must not extensively corrode metallic pens. (6) The writing must rapidly dry and should not be sticky—unless it is a copying ink.

Copying and Hectographic Inks

1. **Writing Inks.**—Ordinary iron-gall and logwood writing inks are rendered capable of giving one or two good copies in a press, or less readily in a rapid-roller copying machine, by the addition of glycerol, gum, sugar, glucose, etc., to a previously concentrated ink.

Better results are obtained by using concentrated solutions of the water-soluble aniline dyes with the addition of a small proportion of glycerol.

Many of the copying inks on the market contain an excess of acids and gums or other thickening substances which are not only unnecessary but actually deleterious.

Any of the basic dyes are suitable for the manufacture of copying inks, the proportion to be used varying with the strength of the dye and the number of copies required: *e.g.*, **Violet Inks**—Methyl Violet 3B; Crystal Violet [B]; Methyl Violet O and III. extra N. **Red Inks**—Eosin, Diamond Magenta; Magenta Powder; Safranine T extra [B]. **Black Copying Ink**—Diamond Green B and G [B] + Diamond Magenta + Chrysoidine. Also aniline black dissolved in alcohol and glycerol.

Hectograph inks are merely concentrated copying inks. Occasionally it is desirable to add a small proportion of alcohol and a very slight excess of a weak acid to prevent thickening due to deposition of the dye.

Typewriter Ribbon Inks.—The manufacture of typewriter ribbons has increased enormously in recent years. There are quite a number of firms who have placed on the market machines for cutting, inking and winding typewriter ribbons; whilst the manufacture and cutting into the required widths of the fabric is a separate branch of the industry.

The firms selling inking machines also provide suitable grinding mills and formulæ for manufacturing the inks.

Typewriter ribbons may be divided into two classes:—

(*a*) **Record or Non-Copying.**—The only really permanent ribbons are those inked with a composition having lamp or a similar carbon black as a basis.

For use on a modern inking machine the lampblack, or in the case of coloured ribbons an aniline lake, is ground in a suitable mill with a non-drying oil, thickened if necessary with petroleum jelly. Occasionally a little volatile solvent such as petrol, carbon tetrachloride, etc., is used to facilitate absorption.

Oil-soluble aniline colours may also be employed for the manufacture of one-colour record ribbons.

(*b*) **Copying Ribbons.**—Copying ribbons are made in several varieties.

Slow-copying, two-sided ribbons, for use with the old-fashioned screw press using damp rags; and one or two sided-rapid copying ribbons for use on machines such as the Roneo Copier using rolls of prepared paper.

The slow-copying ribbons contain a lake or colour and a small proportion of a water-soluble dye, whilst the rapid roller ribbons consist of a strong water-soluble dye ground in a non-drying oil.

It is not necessary to add glycerol or indeed any other substance beyond the oil and dye.

Testing Typewriter Ribbons.—A well-made typewriter ribbon should give fine sharp impressions, exhibit no tendency to fill the type and be cleanly in use and last a reasonable time without losing its writing or copying properties or wearing into holes.

The general character of a ribbon can best be judged by an extended and careful test carried out on the machine for which the ribbon is intended.

For purposes of comparison short definite lengths of the ribbons to be tested should be worked backwards and forwards through the typewriter a stated number of times and the results compared.

If the letter "e" is alone used for this test the type-filling property can also be judged.

To test the life of a ribbon a special testing machine similar to that described in the United States Bureau of Chemistry Bulletin No. 109 revised, p. 51, is necessary.

Some idea of the life of a ribbon can be obtained, however, from the results obtained in the character and filling tests described above.

In order to obtain concordant and comparable results, it is absolutely necessary that the tests should be carried out under exactly similar conditions.

A good copying ribbon should give eight to twelve readable copies from one original. The copying test should preferably be carried out on a "Copier" in order to obtain comparative results.

As a rule one-sided ribbons give neater work and are cleaner to handle than two-sided ribbons and are absolutely non-filling, but the life is somewhat shorter than that of a two-sided ribbon. One-colour record ribbons are always two-sided.

Record ribbons may be tested for resistance to sunlight and chemical reagents if necessary.

As mentioned previously only black record ribbons are absolutely permanent, but for ordinary commercial use a good copying ribbon is generally preferred owing to the convenience of being able to obtain actual copies of the correspondence without using carbon paper.

Unless actually exposed to sunlight or to the action of chemicals both the original and copies are sufficiently permanent for commercial office use.—FRANK B. GATEHOUSE, F.C.S.

Copying Ink Pencils are made by making a paste of powdered graphite and kaolin clay with a very concentrated solution of methyl violet, pressing into **sticks** and drying.

Manifold Copying Apparatus.—The block of *Rosefeld's* apparatus (English Patent No. 2,256, 1879) consists of gelatine, glycerol, molasses or sugar, acetic acid, iron oxide, and sodium bisulphite. The ink is aqueous methyl violet.

The drawback of gelatine beds is that they become ultimately saturated with ink. *Smith's* apparatus (English Patent No. 7,149, 1888) obviates this, as **ink** is sponged or scraped off when used. The slab consists of china clay, starch, glycerol, and water. The ink is an aniline dye in water, alcohol, and hydrochloric acid. Similar pads consist of water (10), dextrine (1½), sugar (2), gelatine (15), glycerol (15), zinc oxide (2). Barium sulphate is sometimes used instead of zinc oxide, while the addition of soap makes the surface smooth and easily washable.

Marking Inks

(*a*) **Natural Vegetable Inks.**—A number of plants give black marking inks. Among these we may mention the **juice** of *Coriaria thymifolia*, a plant occurring in New Granada and New Zealand ("ink plant").

The fruit of the Indian tree, *Anacardium orientale* or *Semecarpus anacardium*—the "marking nut"—yields a juice which when mixed with lime water or alkali marks linen an almost indelible black. Similar inks are prepared from the **Cashew Nut** (fruit of Anacardiaceæ, *A. occidentale*, found in India, West Indies, tropical South America), the *Rhus toxicodendron* (North America), *Rhus venenata* (North America), and *Rhus radicans*.

(*b*) **Chemical Marking Inks—Silver Inks.**—These inks contain a silver salt—usually silver nitrate—the reduction of which within the fibres of the material leaves an insoluble black deposit.

Thus *Dieterich's* marking ink consists of 25 parts silver nitrate and 15 gum arabic in 60 parts ammonia solution, to which are added 2 parts of lampblack or indigo. The ink must be used with a quill pen, and fixed by passing a hot iron over it. With 25 parts of gum it may be used with a rubber stamp.

Aniline Black Marking Ink is obtained by mixing 2 parts aniline black, 40 parts 95 per cent. alcohol, and 2 parts hydrochloric acid; add this to 3 parts shellac in 150 parts of the concentrated alcohol. Not very resistant to alkalis.

Often a solution of india-rubber (in benzene or similar solvent) + aniline or other colours is used; *e.g.*, for black, india-rubber + lampblack + solvent.

Foertsch's Pencil for Glass is made by stirring Prussian blue into a melted mixture of 8 parts white wax and 2 parts tallow, and when nearly cold rolling into a pencil on a slab and covering with a paper case.

Printing Inks

These really are rapidly drying **paints**, consisting of pigments of various colours, thoroughly incorporated with varnish made of boiled linseed oil, rosin oil, or other "vehicles" for paints.

Black Printing Inks are made by mixing lampblack with **varnish**. The proportion and quality of the lampblack varies widely according to the purpose for which the ink is employed, ranging from 20-40 per cent., as shown by annexed table (*Andes*, "Oel und Buchdruckfarben," 1889, p. 239), while occasionally a little blue pigment is added.

	Rotary Machine Ink.	Newspaper Ink.	Book Ink.	Illustration Ink.	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Oil varnish	70-72	76-78	77-79	78	78
Lampblack	30-28	24-22	23-21	20	19
Paris blue	...	...	...	2	2
Indigo	...	...	...	...	1

As regards **Newspaper ink** formerly (and still to some extent) rosin varnish was the vehicle used, made by the destructive distillation of rosin, separated from its water and spirit and from the residual pitch products. Recently heavy mineral oils have largely displaced the resin. Soap is also often added, the presence of soap causing the ink to "lift" well. These vehicles or varnishes are carefully ground with lamp-black, the varnish being made of varying consistencies according as whether the ink is required for slow or fast printing, cold or hot climates. In the inks used now there is a tendency to add blue or blue-black pigments to the lamp-black in order to obtain an intensification of colour and to overcome the brownish tendency which often develops owing to lightness of impression. The exact composition of these inks are carefully guarded trade secrets, but some recipes have been published some of which are given below. In **letterpress inks** the black pigments used are of a more varied character, careful blending of several kinds being resorted to in order to allow the ink to flow at the proper rate for allowing the presses printing machines to run at their proper rate. In **ink for illustrations** the exclusive use of black pigments has now been departed from, delicate shades in ink being now used which greatly heightens the effects of the pictures shown.

The following are some published recipes for printing inks:—

1. To each gallon of **Linseed oil varnish** (prepared by heating the oil to 380°-400° F. in boilers provided with a closely-fitting lid) add 4 lbs. rosin and 1 lb. brown soap in slices. Mix in the proper weight of lampblack (about 30 per cent. of weight of vehicle) or other pigment,

grind and mix in special grinding machinery, between polished granite or steel rollers, then seal up in suitable receptacles, when the ink is ready for use.

2. **Brackenbusch's mineral oil inks** consist of 25 parts paraffin oil, 45 parts of rosin (colophony) and 15 parts of lampblack. For soft inks for high-speed work reduce the percentage of rosin.

3. **Fireman's ink** (U.S. Patent., 802,928) consists of manganese dioxide or oxides of iron pigments ground into varnish. The paper can be bleached and re-made into white paper, which cannot be done with lampblack inks.

The following are some published "*vehicles*" for inks:—

Mineral Oil Vehicles.—Rosin, 1 part, dissolved in 1 part of mineral oil of sp. gr. 0.880 to 0.920, previously heated to expel volatile components.

Rosin Oil Vehicle.—Rosin, 50; rosin soap, 5, dissolved in rosin oil, 50; boiled linseed oil, 50; partly boiled linseed oil, 6.

Linseed Oil Vehicle.—Boiled linseed oil, 100; partly boiled linseed oil, 6; rosin soap, 10; rosin, 50.

Composition Vehicle.—(1) Olein (added hot), 4; soft soap, 10; thick turpentine, 10. (2) White wax, 1 part mixed at 400° C. with castor oil, 15, and Venice turpentine, 5.

Coloured printing inks are obtained by adding pigments to the oil while it is being heated.

Red—Vermilion, madder, Indian red, Venetian red, orange mineral, orange lead, burnt sienna, rose pink, rose red, red lead, are the colours most used. A bright red is got from pale vermilion + carmine. Also orange red and vermilion (very permanent). For **Pink** use carmine or crimson lake. **Blue**—Ultramarine, Prussian blue, Antwerp blue, Chinese blue, indigo. Indigo makes a good dark blue, but is difficult to lighten. Prussian blue dries quickly and hence requires the roller to be often cleaned. Chinese, Antwerp, and Prussian blues are difficult to grind and print greenish with thin varnish. **Purple** = red + blue pigments. **Lilac** = carmine + cobalt blue. **Green**—Mixtures of yellow and blue pigments, also chrome green, cobalt green, emerald green. **Emerald Green** = pale chrome + Chinese blue. Antwerp blue + yellowish varnish gives greenish tints. **White**—Heavy spar (barium sulphate); zinc white, lithophone, white lead. The latter darkens in air. **Yellow**—Chrome yellow, yellow ochre, gamboge. For bright tints use chrome yellow (lead chromates). For dull tints use yellow ochre. **Brown**—Burnt umber + scarlet lake; burnt sienna alone or with scarlet lake. Avoid heavy colours. See **Pigments**, p. 497 *et seq.*

For **Copperplate printing** and **lithographing** thicker ink is used, which is mixed with a denser black than that used in ordinary printing. The varnishes, made with utmost care from linseed oil thickened by extremely high temperatures.

Modern recipes not published. Old recipes are:—(1) wax, 18; shellac, 14; rosin, 7; tallow, 10; soap, 18. Fuse and incorporate 6 of lampblack and 2 of rubber dissolved in 5 of oil of turpentine. (2) Shellac, 12; mastic, 8; turpentine, 1. Melt, and add 16 wax and 6 tallow, mix well and incorporate 4 of lampblack. For an **autographic ink**, melt white wax, 8; white soap, 2.5; incorporate 1 of lampblack, heat strongly and mix in 2 of shellac. Heat again.

The author desires to thank Mr J. W. Barker, A.R.C.S., B.Sc. (H.M. Patent Office), for looking through the MS. of inks and giving me many suggestions. Also Mr Frank B. Gatehouse, of Messrs Roneo, Ltd., for supplying some details of hectographic and copying inks.

Statistics.—The United States imported *Ink* and *Ink powders* to the value of $75,000 in 1906, and $44,000 in 1910. The figures for 1910 are:—

Printers' ink	$4,787.
Writing and copying ink	19,416.
All other, including ink powders	20,162.

The United States exported (principally to England, Canada, and Mexico):—

	1906.	1910.
Printers' ink	$275,000.	$326,000.
All other	174,000.	192,862.

The British import of printers' ink in 1913 was £23,000. In 1907 Great Britain made £536,000 of printers' ink and £69,000 of other inks (writing, endorsing, marking, etc.).

SECTION XVI

The Paint and Pigment Industry

THE PAINT AND PIGMENT INDUSTRY

By J. Newton Friend, D.Sc., Ph.D.

LITERATURE

For a more complete account of the pigments in common use the reader may be referred to "An Introduction to the Chemistry of Paints" by J. Newton Friend (Longmans & Co., 1910). Also the following:—

Zerr and Rübenkamp.—"A Treatise on Colour Manufacture." Griffin & Co., 1908.
Hurst.—"Painters' Colours, Oils, and Varnishes." Griffin & Co., 1906.
Eibner.—"Malmaterialkunde." Berlin, 1909.
Gentele.—"Farbenfabriken." Brunswick, 1906.
Toch.—"Chemistry and Technology of Mixed Paints." 1907.
Church.—"Chemistry of Paints and Painting." Seeley & Co., 1901.
Wrigit.—"Simple Methods of Testing Painters' Materials." Scott, Greenwood, & Son, 1903.
Laurie.—"Materials of the Painters' Craft." Foulis, 1910.
Jennings.—"Paint and Colour Mixing." Spon Ltd., 1906.
Holley.—"Lead and Zinc Pigments." Chapman & Hall, 1909.

PIGMENTS

The Chemistry of Pigments is a study of supreme importance—a fact which painters and manufacturers have only recently begun to appreciate. In the present section the limitation of space prevents our doing anything like full justice to the subject, but an attempt is made to lay before the reader the main outlines in question; for further detail reference should be made to the works cited above.

Pigments may be classified according to several different schemes. Thus, for example, the painter groups his pigments from the point of view of colour. The chemist, on the other hand, considers their chemical composition. Here, again, two methods are possible. We may group the pigments according to the chemical nature of their bases, or of their acid content. Neither system is perfect, but we shall adopt the former in these pages.

Pigments Containing Lead

White Lead.—One of the oldest and most important pigments belonging to this group is white lead or lead carbonate. It was known to the Romans and Greeks at the beginning of the Christian era, the pigment being obtained from the mineral cerussite, in which form lead carbonate occurs in nature. The modern painter, however, employs the artificial product only. Although numerous methods have been invented and patented for the manufacture of white lead, the best results are apparently yielded by the old *Dutch Process*, which we will therefore describe first.

Several thousand earthenware pots are about one-third filled with a 2-3 per cent. solution of acetic acid, and are built up into stacks inside large sheds specially built for the purpose. The method of working is as follows: The floor of the shed is spread with spent tan, and upon this a layer of crucibles is set, and covered with perforated sheets of lead, known as "blue lead." Wooden boards are now laid on the top, and these in turn are covered with tan, carrying another layer of pots, and

so on, until the numerous layers have completely filled the sheds. The whole is now left alone for a period varying from three to four months, according to circumstances. During this time the tan ferments, and the heat thus liberated serves to vaporise the acetic acid in the pots. The leaden sheets are thereby converted by degrees into lead acetate, which in turn is decomposed by the water vapour and carbon dioxide (evolved from the decaying tan) yielding lead carbonate. On opening the stack the sheets are scraped, and after washing and crushing (which flattens out any unchanged blue lead, and renders it easy to separate) the pigment is ready for the market.

According to Liebig the following successive changes take place :—

1. $$Pb + 2CH_3.COOH = Pb(CH_3.COO)_2 + H_2.$$

2. $$2Pb(CH_3.COO)_2 + 2H_2O = \underset{\text{Basic lead acetate.}}{Pb(CH_3.COO)_2.Pb(OH)_2} + 2CH_3COOH.$$

3. $$\underset{\text{Basic lead acetate.}}{3Pb(CH_3.COO)_2.Pb(OH)_2} + 4CO_2 = \underset{\text{White lead.}}{2(2PbCO_3, Pb(OH)_2)} + \underset{\text{Acetic acid.}}{6CH_3COOH}.$$

The acetic acid liberated then attacks more lead, thus repeating the cycle of operations. According to more recent views no hydrogen is evolved (see 1), the acetic acid merely serving to dissolve lead hydroxide formed by the action of air and moisture on metallic lead, thus :—

1. $$Pb + H_2O + O = Pb(OH)_2.$$

2. $$Pb(OH)_2 + 2CH_3.COOH = Pb(CH_3.COO)_2 + 2H_2O.$$

The lead acetate then combines with the lead hydroxide, forming basic lead acetate :—

$$Pb(CH_3.COO)_2 + 2Pb(OH)_2 = \underset{\text{Basic lead acetate.}}{Pb(CH_3.COO)_2, 2Pb(OH)_2},$$

which is then decomposed by the CO_2, producing white lead according to the equation (3) above.

The following processes for the manufacture of white lead are important :—

The German or Chamber Process, said to be rapidly displacing the other processes, is carried out by suspending 6·20 tons of pure lead in the form of sheets or grids from the roof of a series of chambers provided with flues whereby the admission of air can be regulated. Vinegar vapour, evolved from pans which are placed below the chamber and in which dilute vinegar is heated, is led into the chamber, together with a carefully regulated supply of aqueous vapour, air, and carbon dioxide—the latter being produced by burning charcoal or coke in stoves—and the temperature of the chambers is maintained at 60°-80° C. for eight to ten weeks, when the lead plates are converted into white lead. The quality of the product is good, and stated to be equal to the best white lead prepared by the old Dutch method.

In the Clichy or French Process, lead monoxide (litharge) is dissolved in vinegar to form basic acetate (1 molecule of acid dissolving 3 molecules of PbO), then CO_2 is passed through the clear solution for about twelve hours; most of the lead is precipitated as carbonate, but part remains dissolved as neutral lead acetate. The precipitate of "white lead" is filtered off, more PbO is dissolved in the clear filtrate, CO_2 again led in to precipitate it, and so on. The great advantage of this method is its quickness. The product, however, is variable in quality and inferior to that of either of the processes mentioned above.

Brown's Electrolytic Process.—A solution of sodium nitrate containing about 1 lb. of the salt to the gallon is placed in a series of wooden cells, each of which is provided with a porous partition. A strong electric current is passed through the solution, a pig lead forming the anode in each cell, and a sheet of copper the cathode. Nitric acid is liberated at the anode, and attacking the lead forms lead nitrate, which passes into solution. Sodium hydroxide is formed at the cathode: it has no effect on the copper plate. The two solutions are drawn off separately and mixed in quantitative proportions, when they react to form lead hydroxide and sodium nitrate thus :—

$$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3.$$

The sodium nitrate is used again as a source of nitric acid and sodium hydroxide,

and the lead hydroxide is treated with a solution of sodium bicarbonate with the formation of white lead and sodium hydroxide, thus :—

$$3Pb(OH)_2 + 2HNaCO_3 = 2PbCO_3, Pb(OH)_2 + 2NaOH + 2H_2O.$$

The white lead is separated from the sodium hydroxide and carbon dioxide passed through the latter, thus converting it into sodium bicarbonate for further use.

This is an extremely rapid method of making white lead. The product is highly amorphous in character, and is said to be equal to the best white lead produced by the Dutch method.

Properties of White Lead.—White lead mixes extremely well with oil, and possesses unusually good body, spreading power, and durability. There are, however, two serious drawbacks to its use, namely, the tendency to blacken in the presence of sulphur compounds, and its extremely poisonous nature. When worked in oil white lead loses, in the course of a few months, a little of its opacity, a peculiarity which is probably due to the oil combining with the pigment to form a translucent lead soap.

White lead varies somewhat in composition and character. It should, however, have the composition $2PbCO_3, Pb(OH)_2$—that of the best white lead produced by the Dutch method—and any departure from this leads to a loss of body if the $Pb(OH)_2$ be in excess, and to inability to form a proper emulsion with linseed oil if the $PbCO_3$ be in excess.

The cheaper grades of white lead are adulterated, often to a very large extent, and sometimes contain no lead carbonate at all. The most usual adulterant is barytes—barium sulphate—others commonly used are lead sulphate, china clay, and whiting—impure calcium carbonate—and sometimes strontium or barium carbonate, magnesite—magnesium carbonate—and zinc oxide, etc., may be found.

Red Lead rivals even white lead in age and importance. It is found in nature as the mineral minium, but, as in the case of white lead, the modern painter uses the manufactured article only.

This is prepared by heating metallic or "blue" lead in a current of air, whereby lead monoxide is formed. This is removed and ground, any particles of unoxidised metal being thereby flattened out, and thus easily removed by means of sieves. On further heating in excess of air for forty-eight hours the monoxide combines with more oxygen and yields triplumbic tetroxide (Pb_3O_4), commonly known as red lead. These changes may be represented by the following equations :—

$$6Pb + 3O_2 = 6PbO$$
$$6PbO + O_2 = 2Pb_3O_4.$$

In practice 100 lbs. of blue lead yield about 108 lbs. of red lead.

Properties of Red Lead.—Red lead mixes readily with the drying oils and rapidly sets, and on this account is largely used by plumbers for packing and luting pipes, etc. Although very permanent and inert in all ordinary circumstances it is subject to the same defect as white lead, namely, that it blackens in the presence of sulphur or sulphur-containing bodies. It cannot, therefore, be safely mixed with such pigments as lithopone and ultramarine. Occasionally it is adulterated with venetian red (Fe_2O_3), the presence of which is easily detected in the following manner :—

The pigment is subjected to prolonged warming with concentrated nitric acid. If any insoluble residue remains, the presence of silica or sand is to be suspected. If the solution is yellow, the presence of iron may be inferred. Addition of excess of dilute sulphuric acid will cause the precipitation of white lead sulphate, the iron still remaining in solution. On filtering and adding to the filtrate a few drops of potassium ferrocyanide the presence of iron is betrayed by the immediate production of a deep blue colour—Prussian blue.

Lead sulphate forms the basis of a large number of pigments known variously as **non-poisonous white lead, patent white lead,** sublimed white lead, and the like. Although lead sulphate occurs in nature as the minerals **anglesite** and **lanarkite,** these latter are seldom used for the production of the pigment. Manufacturers prepare it by the addition of dilute sulphuric acid to the strong aqueous solution of lead acetate obtained by treating granulated lead with acetic acid. Thus :—

$$Pb(C_2H_3O_2)_2 + H_2SO_4 = PbSO_4 + 2H.C_2H_3O_2.$$

The acetic acid thus liberated is used over again in the production of fresh lead acetate. The precipitated sulphate is allowed to settle, after which it is washed and dried.

Although less poisonous than lead carbonate, lead sulphate has never been as great a favourite amongst painters because its body and spreading power are inferior. It is less sensitive to the action of sulphur than white lead, but it is not advisable to mix it with such pigments as ultramarine and lithopone for obvious reasons.

A basic lead sulphate is being manufactured at Greenford under the name of **Purex** direct from galena or lead sulphide, by combustion in a current of air, whereby oxidation takes place. The resulting compound varies in composition between the limits $2PbSO_4.PbO$, and $3PbSO_4.PbO$. It is claimed to be practically non-poisonous (see *The Decorator*, 1911, 9, 251).

Owing to the particular method of preparation—namely, production in the vapour state, and subsequent deposition as a solid without the intermediate formation of a liquid—the pigmentary particles are unusually fine, and thus admit of thorough admixture with oil in preparing paints. This results in the production of paint of exceptional spreading power, but somewhat lacking in body or opacity. In many cases this is not a matter of importance, but for those cases in which opacity is essential the manufacturers recommend a special brand of their Purex in which this objection has been overcome.

Turner's yellow is an oxychloride of lead, and appears in the market under many names, such as **Patent yellow, Cassel yellow, Verona yellow, Montpelier yellow, Mineral yellow,** etc. It is usually prepared by mixing litharge to a thin paste with a solution of common salt, when the following reaction takes place :—

$$PbO + 2NaCl + H_2O = PbCl_2 + 2NaOH.$$

In about twenty-four hours' time the reaction is fairly complete, the mixture becoming white in consequence of the lead chloride. It is dried, transferred to a crucible and heated to melting until the desired hue has developed.

Turner's yellow possesses good body and mixes well with the drying oils. Of late years, however, it has decreased in popularity in consequence of the extensive rise of the chromes.

Chrome yellow or lead chromate is prepared by the addition of potassium bichromate to solutions of lead acetate (see p. 559). Thus :—

$$K_2Cr_2O_7 + 2Pb(C_2H_3O_2)_2 = 2K(C_2H_3O_2) + 2PbCrO_4 + 2H.C_2H_3O_2.$$

Slight variations in the method of manufacture cause marked differences in the hue of the resulting product. Warming with an alkali converts it into the basic chromate, which is orange or red according to circumstances. It is then known as **Orange chrome, Chrome red, Derby red, Chinese red,** etc. All of these pigments, however, are subject to the general fault of lead compounds, in that they are rapidly discoloured in the presence of sulphur or of sulphur compounds.

Pigments Containing Iron and Cobalt

Some of our commonest and most permanent and useful pigments are compounds of iron.

Ochre, Sienna, Umber.—These pigments consist of the hydrated oxide of iron, in the case of sienna and umber a little manganese being present in addition, which probably explains their darker colour. Umber was first found near the ancient Italian town of *Ombria*, now known as *Spoleto*, whence its name; the best umbers, however, hail from Cyprus but are known in the trade as Turkey umbers since they were originally shipped from Constantinople, their real source being at the time unknown. Sienna was likewise first found near an Italian town bearing the same name. Both ochres and umbers are found in this country—Cornwall, Derbyshire, and Oxfordshire—in Wales, Italy, France, Australia, and the New World.

The methods of preparing these natural deposits for the use of the painter vary somewhat according to their source. The ochres are first ground if they are hard, but this process is omitted if they are soft. They are then levigated, or mixed with water and allowed to settle in large tanks. The coarser particles obviously fall to the bottom first, and if the supernatant liquid is poured off, and again allowed to settle, the sediment will this time be considerably finer. Repetition of this process for some four or five times will clearly yield a pigment of very varying grades of quality. It is usually found that the depth of colour of the ochre varies considerably according to the degree of fineness, the finest ochres being the palest. The sediment obtained in this way contains about 50 per cent. of water and is dried by the aid of gentle heat. If the temperature is allowed to rise too high the ochres develop a ruddy hue owing to their partial conversion into the anhydrous oxide, known as rouge or red oxide.

Umber is frequently sent into the market direct from the mine without any treatment. It is then known as ordinary "raw umber." If it is first levigated it is styled "powdered raw umber." Sienna is not usually levigated, but it may be ground if necessary. These pigments are very inert from a chemical point of view, and are therefore characterised by their durability and permanence. Somewhat similar pigments to the above are **Vandyke brown** and **Cappagh brown**. The former received its name in honour of the great painter who is known to have been particularly attached to the liberal use of browns, whereas the latter is from the district in Cork, Ireland, where it is mined. Vandyke brown contains a fairly high percentage of organic matter, and is greatly prized on account of its transparency, which enables it to be painted over the surface of other pigments, producing beautiful tones. According to Church (*q.v.*, p. 206) Cappagh brown contains approximately 27 per cent. of manganese oxide.

Rouge.—Mention has already been made of the fact that, if the ochres are overheated during the drying process, they are converted more or less completely into **rouge**, the anhydrous oxide of iron, Fe_2O_3, owing to the expulsion of the combined water of hydration. This is one of the methods by which the various red iron oxide pigments are prepared. The ochre is heated in specially constructed furnaces for varying lengths of time or at different temperatures according to the particular depth of colour required. The resulting products are known variously as **Indian red, Venetian red, Red oxide, Rouge**, etc. In a similar manner sienna and umber yield **Burnt sienna** and **Burnt umber**.

The anhydrous oxides of iron are also prepared by calcining ferrous sulphate or copperas, $FeSO_4.7H_2O$, obtained by the atmospheric oxidation of iron pyrites (FeS_2) in the presence of moisture and scrap iron. The changes taking place during the weathering may be represented as follows:—

$$FeS_2 + Fe + 4O_2 + 14H_2O = 2FeSO_4.7H_2O,$$

and during calcination:—

$$2FeSO_4.7H_2O = Fe_2O_3 + 14H_2O + SO_2 + SO_3.$$

A third method of preparing the anhydrous oxides of iron is afforded by the fact that in many manufacturing processes large quantities of iron salts are produced as waste products. From these the brown hydrated ferric oxide is precipitated by

the addition of alkali (soda, ammonia, or lime) and heated to redness in crucibles in a similar manner to the ochres.

These red oxides are very valuable pigments, being characterised by their inertness and permanence. They do not mix so well with oil as red lead, neither do they act as driers. They are particularly valuable in the preparation of paints for the coating of iron work and the like. The Maori use a variety of rouge for decorative purposes under the name of *Kokowai*.

Terre verte is a green earthy pigment found in the Mendip Hills, and in several other European countries. It consists essentially of silica and oxide of iron, small quantities of other oxides being usually present as well, together with from 6-8 per cent. of water.

Siderin yellow is a basic chromate of iron, and finds a limited application as a water colour. It is prepared by heating solutions of ferric chloride and potassium bichromate.

Prussian blue (p. 559), known to the chemist as ferric ferrocyanide, $Fe_4(FeC_6N_6)_3$, was discovered accidentally by Diesbach, a German colour manufacturer, in 1710. It is characterised by its intense colour, a single pound of it sufficing to give a perceptible tinge to over 600 lbs. of white lead. It is prepared by adding potassium ferrocyanide (yellow prussiate of potash) to a ferrous salt which has been oxidised to the ferric condition with bleaching powder. Obtained in this way the pigment is known as **Chinese blue**. Commoner makes enter the market as **Prussian blue, Berlin blue, Paste blue**, etc., and ordinary alum is one of the ingredients used in their preparation. In manufacturing **Antwerp blue** both alum and zinc sulphate are employed. **Brunswick blue** is an admixture of Prussian blue with barytes and silica or some other insoluble white pigment. The great drawback to the use of this composition is the tendency exhibited by the heavy barytes to settle to the bottom, the blue remaining suspended in the supernatant oil.

Prussian blue is unusually difficult to grind in a drying oil owing to a curious tendency to "leather" or "liver," that is, to set up to the consistency of leather. This difficulty is usually overcome by paint grinders by the use of special mixtures or blends of oil in which this peculiarity is shown to a minimum extent. Being insoluble in dilute mineral acids, Prussian blue is very permanent in certain acid atmospheres. Alkalis, however, readily decompose it, forming red ferric hydroxide. Warming with oxalic acid solution effects its solution, the resulting liquid being used extensively at one time as an ink. More recently, however, aniline dyes have tended to replace this older product. When used as a water paint, Prussian blue fades slowly on exposure to light, but the colour returns to its original intensity after prolonged darkness. Owing to its intense staining properties, Prussian blue is seldom used alone. Mixed with barytes and chrome yellow the so-called **Chrome greens** or **New Brunswick greens** are produced, which possess good body and colouring power, and work well both in oil and in water. When the chrome yellow in these pigments is replaced by zinc chrome, the so-called **Zinc greens** are produced. These are very popular on account of their relatively low cost and their brightness. An astonishing variety of hues, tints, and shades can be produced by suitably adjusting the proportions of their several constituents, which is a great advantage. Zinc greens are more apt to "run" or "blue" than the chrome greens, and they possess a slightly inferior body. On the other hand they are more permanent, since zinc chromate itself is more stable than chrome yellow.

Armour-scale Paints form a numerous and very variable class of grey paints. They all consist mainly of micaceous iron ore, generally admixed with the common red oxide of iron and gangue, and more or less graphite. There should be no rosin, rosin-oil, driers, or turpentine present. The colour of these paints is very variable, though it is generally some shade of grey. The specific gravity also varies considerably; it is, however, higher than that of graphite or silica-graphite paints, and lower than that of most other paints.

Smalt is a potash glass containing oxide of cobalt instead of lime. It is prepared by mixing zaffre (the technical name for cobalt oxide) with powdered quartz and potassium carbonate, and subjecting to a white heat in clay crucibles. On throwing the fused mass into water, disintegration into small angular pieces takes place. These are ground, levigated, and dried. Although very permanent, the colouring power of smalt is weak. This defect, together with its cost, has decreased its popularity amongst painters of late years.

Cobalt blue is prepared by heating to redness the precipitated oxides of cobalt and aluminium, and is used largely by water-colour artists. Its extreme permanence and resistance to the attacks of acids and alkalis have caused it to be used for superior decorative purposes.

Cobalt green is similar to cobalt blue, zinc oxide taking the place of alumina. It is also known as **Rinmann's green** and **Zinc green**, but its use is limited owing to its cost.

Pigments Containing Copper

With the exception of copper chromate, the copper pigments are possessed of a green or blue colour, and were for many years highly prized. They are not very permanent, however, and are all blackened by sulphuretted hydrogen, owing to the formation of black copper sulphide CuS, which renders their use subject to the same limitations as the lead pigments. Moreover, many of the pigments are blackened by heat owing to their decomposition to black copper oxide.

One of the most interesting of the copper pigments is the basic acetate, popularly styled **Verdigris**, and which is manufactured in several ways. The old French method consists in exposing scrap copper to the action of grape skins discarded from the vineries. These skins, on fermenting, produce acetic acid which attacks the copper, converting it into the acetate. After two or three weeks sufficient verdigris has formed to be worth scraping off. The greenish blue colour of verdigris is familiar to all. In oil it is usually more permanent than in water. When strongly heated, black copper oxide results, so that due care must be exercised in drying the pigment. It dissolves readily in dilute acids without effervescence. Should an evolution of gas occur, the presence of some carbonate impurity is to be suspected. If a white residue remains, barytes, silica, etc., are probably present. Should the residue be blue, the probability is that Prussian blue is present; confirmation is afforded if the mass becomes brown on addition of caustic soda (see **Prussian blue**, above).

Lime blue is essentially a mixture of calcium sulphate and copper hydroxide, and is prepared by adding milk of lime to a solution of copper sulphate containing excess of ammonia. Some years ago, before ultramarine could be prepared in a cheap way artificially, lime blue was in great demand for frescoes and colour washing. In common with all copper and lead pigments, however, it is discoloured by contact with sulphur, and may not, therefore, be mixed with such bodies as cadmium yellow, ultramarine, and the like.

Scheele's green is now antiquated, and rightly so, on account of its poisonous properties, being a compound of the oxides of copper and arsenic. **Emerald green** is an aceto-arsenite of copper, and may be prepared by mixing equal quantities of white arsenic and verdigris with water, and allowing to stand. Other names for this pigment are **Paris green** and **Schweinfurth green**.

A basic carbonate of copper is found as the mineral **malachite**, $CuCO_3.Cu(HO)_2$, in Cornwall, Yorkshire, and other parts of Great Britain. When finely ground it is used as a pigment under the names of **Mineral** or **Mountain green**. Azurite

is another basic carbonate of copper to which the formula $2CuCO_3.Cu(HO)_2$ is usually given. This yields the **Mountain blue** of the painter.

Bremen blue is an artificial product obtained by intimately mixing copper carbonate with an excess of copper hydroxide. **Blue verditer** is a basic carbonate of copper, prepared by mixing together solutions of copper sulphate and sodium carbonate. It is used by water-colour artists to a limited extent, but is not very permanent. The so-called "Refiners' Blue Verditer" is just the same thing, but has been prepared from copper solutions obtained in the refining of silver and gold —hence its name.

Old Brunswick green was, strictly speaking, a basic chloride of copper, now rarely manufactured. The term, however, is misleading, both Emerald green and Bremen blue being known by this name as well.

Copper chromate is a brownish red pigment prepared by the action of potassium chromate upon a soluble copper salt. It is seldom used.

Pigments Containing Aluminium

Metallic aluminium, usually mixed with zinc, in the form of a fine powder is frequently used as a pigment for painting iron work, and widely divergent opinions are held as to its value.

China clay or Kaolin is a silicate of aluminium to which the formula $Al_2O_3.2SiO_2.2H_2O$ is given, and is formed in nature by the weathering of felspar, itself a decomposition product of granite. It is found in Cornwall and receives extensive application in the manufacture of "china"—whence its name.* It is used largely in distemper work, and owing to its cheapness is rarely adulterated. As an oil pigment it is a failure, since it loses much of its body when mixed with oil.

The only other pigment belonging to this group is **Ultramarine**, which has for centuries enjoyed a world-wide reputation amongst painters. Originally it was obtained from the rare mineral "lapis lazuli," the sapphire of the ancients, which is found in small quantities in Persia, China, Siberia, and South America. The price, however, was prohibitive, the pigment being listed at eighty shillings per ounce a century ago. At the present time ultramarine is manufactured in two ways, designated as the Direct and the Indirect methods respectively.

a. The Direct Method.—A finely ground mixture of—

Kaolin	31·5
Sodium carbonate	28
Sulphur	34·5
Charcoal	6
	100

is heated for several hours at a bright red temperature. On cooling the burnt mass is removed, ground, and levigated. The finer qualities are used in different kinds of printing, the coarser being reserved for the painter.

b. The Indirect Method is conducted in two stages, comprising calcination and "colouring." The actual constituents of the mixture to be calcined depends upon

* White pottery was imported from China before kaolin was known to occur in the British Isles, and was called "china" in consequence. When kaolin was discovered in Cornwall and was used for making similar white pottery it received the name China clay.

the nature of the product required. Thus, for sulphate ultramarine the following mixture is used: *—

	I.	II.	III.
Kaolin	50	47	26
Sodium sulphate	41.5	19.5	57
Coal	8.5	8	...
Sodium carbonate	...	19.5	...
Sulphur	...	6	8
Rosin	...	...	9
	100	100	100

For soda ultramarine rich in silica:—

	I.	II.
Kaolin	33.0	33.3
Silica	3.5	...
Sodium carbonate	36.5	30
Sulphur	22.5	33.3
Coal	4.5	1.3
Rosin	...	2
	100	100

For soda ultramarine poor in silica:—

Kaolin	36.5
Sodium carbonate	36.5
Coal	4.5
Sulphur	22.5
	100

One or other of these mixtures is heated for from seven to ten hours in a furnace, after which it is washed and ground as finely as possible to assist in the extraction of all the soluble matter. This product is known as **Green ultramarine**, and is used by water-paint manufacturers, constituting **Lime green**. In order to convert this green product into blue ultramarine, it is heated again, this time with sulphur. On cooling and grinding the pigment is ready for the market.

What the chemical changes may be which take place during these operations is very uncertain, and until they are understood better we can scarcely hope to discover a more satisfactory method of preparing the pigment.

As a pigment ultramarine is fairly stable, particularly so in contact with alkali, and thus forms a marked contrast to Prussian blue. It is, therefore, used largely in the colouring of distempers, etc., for which Prussian blue is obviously unsuited. Acid soon attacks it, however, liberating sulphuretted hydrogen. For this reason, pigments containing lead or copper may not be safely mixed with ultramarine, as darkening is sure to occur.

Pigments Containing Carbon

Carbon is largely used as a pigment owing to its remarkable permanence and inertness. **Carbon black** or **Charcoal black** is made by heating wood in closed retorts to a high temperature, the resulting mass being ground and washed. **Frankfurt** or **Drop black** is prepared similarly from vine twigs, bones, ivory, etc. The ground carbonised product is mixed with glue water and sent into the market in the form of tears or drops—whence the name, "drop" black. **Ivory black** should be made only from ivory cuttings, but the pure pigment is rare, owing to the high cost of ivory. **Animal black** is prepared by carbonising all kinds of animal matter (leather, horn, hoofs, skin, etc. etc.), and its composition is in consequence subject to variation. In the preparation of **Bone black**, animal bones alone are supposed to be used.

* See p. 78, "Introduction to the Chemistry of Paints," by J. Newton Friend (Longmans & Co., 1910).

Lampblack contains the highest proportion of pure carbon, and is a valued pigment. In order to prepare it heavy oils are heated in a pan, and afterwards ignited in a limited supply of air. The soot is collected in suitable chambers divided into series of compartments by partitions, and at regular intervals workmen enter the chambers and scrape away the pigment. A yield of 30 per cent. is regarded as satisfactory. A variety of lampblack bound with size and containing small quantities of camphor, musk, and possibly sepia, is known as **Indian ink**. The method of manufacture, however, is kept secret.

A complete analysis of the carbon blacks would be very difficult to effect, and is seldom required. The free water is usually estimated by heating a portion of the pigment in a steam oven (or hot-air oven at 110° C.) until constant in weight. The residue is ignited in a crucible until only a whitish ash remains, and the percentage of volatile carbonaceous matter and non-volatile ash calculated from the results. Such an analysis is sufficient for most purposes.

Graphite paints are chiefly used for the protection of iron and steel structures. They are usually of a grey colour, but are sometimes toned up by red lead, iron oxide, or other highly coloured pigments, thus giving red, brown, or green shades. These paints may be divided into graphite, silica-graphite, and armour-scale paints.

Graphite paints are generally made from naturally occurring graphite ores containing iron oxide, alumina, silica, etc., the percentage of graphite varying from about 25-45 per cent. They are heated to expel the water which is always present to a small amount and then finely ground. They are then ready for use.

An artificially prepared graphite has recently been introduced under the name of "Acheson graphite." This is prepared by heating anthracite coal and sand for several hours in an electric furnace. The silica (sand) is first reduced to silicon, which then unites with excess carbon to form silicon carbide or carborundum. Thus :—

$$SiO_2 + 3C = SiC + 2CO.$$

As the temperature is raised the silicon carbide dissociates, the silicon volatilising and leaving the carbon behind in the form of graphite. Thus :—

$$SiC = Si + C.$$

The advantage of this process is that the graphite obtained is exceptionally pure, since at the temperature of its formation all impurities volatilise. The product is broken up and graded. That used for the manufacture of paint is ground to an extremely fine powder, and air floated for collection.

Graphite paints have a soft grey tint—when left of the original colour—and are of very low specific gravity. They are readily adulterated—especially by means of steatite—and are sometimes found to contain no graphite at all.

Silica-graphite paints vary greatly in composition. They should consist of a mixture of graphite and silica, but are frequently adulterated with steatite, barytes, furnace-slag, red lead, iron oxide, etc., in the same manner as graphite paints. These paints closely resemble graphite paints in colour and specific gravity.

Pigments Containing Barium, Strontium, Calcium, and Magnesium

One of the most important of these is **Barium sulphate**, known variously as **barytes** and **permanent white**. It is characterised by its extreme insolubility in all the ordinary reagents, acids and alkalis having no effect upon it. It may easily be prepared by adding dilute sulphuric acid to solutions of any soluble barium salt. Barium sulphate occurs in nature as the mineral **barytes** or **heavy spar**. These are crushed and washed in the usual way. As iron compounds are not infrequently present, the crushed ore isusually treated with acid which dissolves out the iron, but leaves the barytes unattacked. Barytes possesses inferior body to white lead, but it mixes well with oil. A particle of the substance held on the end of a platinum wire, moistened with strong hydrochloric acid and introduced into the tip of a Bunsen flame, imparts to the latter a characteristic yellowish green hue. By means of this test the presence of barium salts may readily be detected.

Calcium sulphate is used as a pigment under the names of **Terra alba, Mineral white,** etc. As **Gypsum** it occurs in many parts of England, and this, when ground, yields a very durable and useful pigment. Mixed with hydrated aluminium oxide, the so-called **Satin white** is produced, which possesses superior body. Calcium salts impart a red colour to the Bunsen flame. **Strontium sulphate** is very similar to gypsum, and is occasionally used as a pigment under the name of **Strontian white.**

Barium chromate, variously known as **Barium chrome, Lemon chrome,** and **Yellow ultramarine,** is prepared by acting upon a soluble barium salt with potassium chromate. Thus :—

$$K_2CrO_4 + BaCl_2 = 2KCl + BaCrO_4.$$

Potassium bichromate cannot be used, otherwise the barium salt is kept in solution by the free acid, thus :—

$$K_2Cr_2O_7 + 2BaCl_2 + H_2O = 2KCl + 2BaCrO_4 + 2HCl.$$

Barium chrome has a pale yellow colour, which is very permanent. It is not often used as a pigment, however, being too pale for most purposes, and lacking in body.

Calcium carbonate is better known to the painter as **Whiting, English white, Spanish white,** and **Paris white.** It is seldom used as an oil colour, partly because it assumes a dirty grey shade, but principally because its lightness and porosity cause it to absorb so much oil that its opacity is almost lost. Mixed with linseed oil it yields putty. **Gilders' whiting** is simply a superior quality of whiting. **Magnesite,** the carbonate of magnesium, is occasionally used as a pigment.

Pigments Containing Zinc and Cadmium

Zinc oxide is now being used by painters with increasing favour under the names of **Zinc white** and **Chinese white.** It is manufactured from metallic zinc, which is thrown into white-hot retorts made of fireclay. The vapours issuing from the mouth of the retorts are caught in a current of air and burn with a smoky flame, the fumes being collected in special chambers and used direct as a pigment. A similar method is in use for the preparation of zinc oxide direct from the ore without necessitating the isolation of metallic zinc, which is a costly process. It is stated that 85,000 tons of the pigment, containing over 98 per cent. of zinc oxide, are now being manufactured in the U.S.A. in this way.

When of good quality, zinc white is very pure, fine, and easily worked. Being quite insoluble in oily water and turpentine, it is gradually replacing white lead for many purposes, for it is not so poisonous, and is permanent in the presence of fumes and pigments containing sulphur, in which circumstances white lead is rapidly discoloured. Owing to its cost, zinc oxide is liable to adulteration. Any impurities, however, are readily detected. The pigment is warmed with dilute sulphuric acid. *If pure it should dissolve completely to a colourless solution without effervescence.* This is perfectly characteristic. If effervescence occurs the presence of a carbonate is to be suspected. Should an insoluble residue be left, the presence of silica is to be inferred or some compound of barium, calcium, or lead, which was either present as the insoluble sulphate, or has been converted into such by the sulphuric acid added.

Zinc chromate, Zinc chrome, or **Citron yellow** is prepared by precipitation from solutions of its soluble salts with potassium chromate. Thus :—

$$ZnSO_4 + K_2CrO_4 = ZnCrO_4 + K_2SO_4.$$

The solutions must be neutral, and potassium bichromate cannot be used for the same reason as in the preparation of barium chrome (*q.v.*).

Zinc chrome is used very largely in the manufacture of zinc greens (*vide supra*). Since zinc sulphide is white and not black, zinc chrome is not seriously discoloured by contact with pigments containing sulphur, and in this respect is superior to the corresponding lead chromate—chrome yellow (*q.v.*). It is frequently adulterated with lead chromate, the presence of which may readily be detected by the black colour produced on addition of water containing sulphuretted hydrogen.

Zinc sulphide is rarely used as a pigment alone, but mixed with barium sulphate the well-known **Lithophone** or **Lithopone** is produced. This is used solely as an oil colour, and seems to be regarded with considerable favour by painters generally. Lithopone turns grey in sunlight, and so is unfitted for painting exteriors.

Cadmium sulphide appears in the market as **Cadmium yellow**, and when pure is a most permanent pigment. It is not often adulterated. Admixed with white lead, the so-called "brilliant yellow" is produced. This combination is very unsatisfactory, however, for the white lead gradually discolours owing to the formation of black lead sulphide.

Pigments Containing Chromium and Manganese

The only compound of chromium which it behoves us to consider in this section is the oxide Cr_2O_3 known variously as **Chrome green** and **Guignet's green**. Of these terms the latter is the better, as the former is frequently used for designating the greens produced by mixing lead chromate and Prussian blue (*q.v.*). Guignet's green is usually prepared by fusing a mixture of boric acid and potassium bichromate. On cooling, the mass is washed and ground, yielding an extremely permanent and very beautiful pigment.

Manganese dioxide occurs in nature as **Pyrolusite**, and is occasionally used as a black pigment under the name of **Manganese black**. Owing to its expense, relatively to the carbon blacks, and its powerful drying properties, its use as a pigment is greatly curtailed.

Pigments Containing Arsenic and Antimony

Arsenic sulphide or **King's yellow** occurs free in nature as the mineral **Orpiment**, the "*auri pigmentum*" of the Romans—whence its name. Owing to its poisonous properties it is not now held in great favour. **Antimony sulphide** or **Antimony vermilion** is very similar in its properties, but these two pigments have been largely superseded by the chromes.

Pigments Containing Mercury

The only pigment belonging to this group that demands our attention is **Vermilion** or mercury sulphide, which has been regarded with great favour from very early times. The Egyptians are known to have used it 400 years B.C., and it was greatly prized by the Greeks and the Romans. In those times, however, the pigment was obtained by grinding the mineral **cinnabar**, which occurs in China, Japan, Austria, Spain, and the New World. At the present time, vermilion is prepared exclusively from the artificial product.

One of the earliest methods of manufacturing vermilion is that known as the Dutch Process, and is effected in two stages. A mixture of mercury and sulphur is gently heated in an iron pot, whereby combination gradually takes place, and black mercuric sulphide results. This mixture, which is known technically as "ethiops," has now to be "coloured." To this end it is thrown in small quantities

at a time into red-hot earthenware crucibles fitted with lids. After some thirty-six hours the crucibles are cooled, and the vermilion, which has sublimed to the lids and upper and cooler parts of the crucibles, is removed.

The Idrian method consists in thoroughly mixing 20 parts of sulphur with 105 parts of mercury in wooden barrels rotating some sixty times per minute for about three hours. The resulting mixture should not reveal any globules of mercury when examined with a lens. It is then charged into pear-shaped sublimation pots of cast iron, each of which holds 130 lbs., and is gently heated, whereby black mercury sulphide results. The temperature is now raised and the vermilion sublimes into receivers. It is ground in water, boiled with potash to remove any sulphur, washed, and finally dried at 70°-75° C. After sifting it is ready for the market.

The Chinese process is very similar to this, and if the Chinese vermilion is superior to the European product it is probably because more care is taken by the patient Chinaman in carrying out the minor details of the process.

Vermilion has a beautiful scarlet hue, which is probably the result of its crystalline structure, for when mercury sulphide is first produced, either by precipitation with sulphuretted hydrogen from solutions of soluble mercury salts, or, as in the above case, by heating the mercury and sulphur together, it is always black and presumably amorphous. It would seem that vermilion exhibits a certain tendency to revert to its black amorphous form if exposed to the action of light, air, and moisture; so that as a water-colour pigment it is not very satisfactory. In oil, however, and particularly under varnish, vermilion is a very stable pigment in most cases. Owing to its unusual density (viz., 8.2) it is apt to settle out of paints, which latter must therefore be constantly stirred during application.

When heated strongly vermilion completely volatilises and should leave less than 1 per cent. of ash. Adulteration is often practised, red lead and rouge being added to it. Their presence, however, can readily be detected both qualitatively and quantitatively by heating the vermilion to redness in a crucible and examining the ash left behind.

Statistics.—The following figures show the amount of the English import and export of pigments:—

	Import, 1910.		Export, 1910.	
	Cwt.	Value.	Cwt.	Value.
Painters' colours and pigments: barytes	908,505	£134,639	229,894	£38,118
,, ,, ,, nickel oxide	17,297	86,150	23	235
,, ,, ,, white lead	288,731	240,372	404,401	401,897
,, ,, ,, zinc oxide	304,183	323,937	38,221	44,595
,, ,, ,, other sorts	860,304	786,167	1,692,465	2,208,460
Total of painters' colours and pigments	2,379,020	£1,571,265	2,365,004	£2,693,305

The United States imported in 1910 paints, pigments, and colours to the value of $1,915,000. The export in 1910 was:—

Carbon black, gas black	$680,000
Zinc, oxide of	956,000
All other	3,090,000
Total	$4,726,000

My thanks are due to Mr Dancaster, B.Sc., Chemist, Engineering Department of the L. & S.W. Railway, for particulars regarding some modern graphite paints, and for notes on certain recent processes of white lead manufacture.

LAKES*

Lakes are compounds of inorganic bodies with organic colouring matter; and during the past few years increasing attention has been paid to their manufacture in consequence of the rapid progress made in the preparation of dyes from coal-tar products. Originally the organic dyes were obtained solely from natural sources, such as, for example, lac dye from the lac insect, cochineal from the *Coccus cacti*, alizarin or madder from the roots of the madder plant (*Rubia tinctorum*), and so on. Almost all of these colours are acidic in character, and yield lakes when neutralised or made to combine with those metallic oxides or hydroxides which are basic in character. On the other hand the artificial dyes prepared from coal-tar products vary so much from one another in their chemical behaviour that different methods have to be employed in manufacturing lakes from them as occasion requires.

Lakes are usually poor driers, but they are characterised by their transparent nature, which makes it possible to use them in glazing or toning in a similar manner to Vandyke brown (*q.v.*). By mixing with some colourless (white) and opaque body such as barytes and gypsum the lakes are likewise rendered opaque, and thus resemble our ordinary pigments.

A. Lakes from Natural Colours

Lakes from natural colours may be readily obtained by simply mixing the dyes with basic metallic oxides or hydroxides in vats. The resulting products are both coloured and insoluble in water—two important qualities essential to pigments. From a theoretical point of view a true lake should resemble a true salt, in that it contains just sufficient of the base as will combine with the colouring matter and no more. In practice, however, it is customary to add excess of the base, with the result that the tint of the finished product is proportionately lighter. In this way a gradation of tints may be obtained.

The most famous and important of the natural colour lakes is **carmine**, a compound of cochineal, lime, and alumina. The details of its manufacture are, however, kept a close secret. Carmine works satisfactorily both as an oil and a water colour, but fades on prolonged exposure to air and sunlight. During the preparation of carmine the metallic base does not effect the precipitation of all the cochineal, so the coloured liquors are mixed with alum, tin chloride, and potassium carbonate, the last named effecting the precipitation of the so-called **Carmine lake**. **Crimson lake** differs from carmine lake only in that it contains a higher percentage of alumina. **Scarlet lakes** are virtually crimson lakes tinted with vermilion.

B. Lakes from Coal-Tar Colours

These are rapidly superseding those obtained from natural sources, as has already been mentioned. For our present purpose we may divide the coal-tar dyes into three classes as follows:—

1. **Acid Colours.**—This name is slightly misleading, for the acid colours are not necessarily of an acid character although such happens to be the case with some of them. The name "acid" colour originates from the fact that it is usual to add some free acid to the colour vats when dyeing wool and silk. The dyes are precipitated from solution by metallic salts; barium chloride, lead acetate, and aluminium sulphate being the three commonly employed.

Acid colour lakes may be used either as oil or water colours, and the results are very permanent.

* For an account of the natural and artificial dyes now used by manufacturers for various purposes, the reader is referred to Sections XIII. and XIV. of this work, especially p. 443.

2. **Basic Colours.**—These yield precipitates with certain weak organic acids, such as tannic acid and picric acid. These precipitates are definite chemical compounds when pure, but in practice the relative amounts of the constituents are varied in order to effect corresponding changes in hue. Unfortunately the organic acids present exert a marked retarding action upon the drying of the oil used as vehicle, so that these lakes are not very suitable for oil paints. They are used as water colours, however, and good results are obtained by varnishing on top of such work.

3. **Mordant Dyes.**—These dyes are generally colourless, but when combined with a "mordant" their colour is developed. The actual colour developed depends very largely upon the character of the mordant used. Thus, for example, alizarin yields a scarlet colour with tin, a bright red with alumina, but a violet with iron.

The resulting lakes are usually very permanent.

DISTEMPERS AND WATER PAINTS

Distempers are made by diluting cheap pigments with water containing a little glue to serve as a binding agent. They are applied to plaster, stucco, brick, and stone. In dry buildings they are very permanent. As a rule whiting is used in this country and coloured with small quantities of ultramarine, indigo, and such-like pigments which are characterised by deep staining properties. Sometimes the whiting is mixed with cheap permanent pigments, such as ochre and rouge, or indeed entirely replaced by these if a deep colour is desired. The pigments are made into a mud with water and size is added until the whole is of the consistency of cream. Occasionally alum is introduced into the mixture, but this is not to be recommended if pigments are used for staining which are susceptible to the action of alum. In America, lime preparations under the name of "Kalsomine" are used in distemper. Owing to the alkaline nature of whiting such pigments as Prussian blue, chrome yellow, etc., may not be used to colour it. The most suitable pigments for this purpose are ochres, umbers, siennas, rouge, lime blue, and indigo. These, alone and in combination, will suffice to yield a fine array of hues, tints, and shades.

The following table gives a list of foreign substances often added to distempers to modify their properties:*—

Substance Added.	Result.
Turpentine, Paraffin	Increased binding power.
Glycerin, Sugar, Treacle	Slower drying.
Carbolic acid, Chloride of lime	Deodorises and disinfects.
Vinegar	Neutralises the alkalinity of the lime. Renders size more fluid.
Alum	Renders size more fluid.
Spirits of wine	Size hardened and rendered less easy to remove.
Soap	Hinders undue absorption.

Water paints are not the same as distempers, although the two names are often regarded as synonymous. Water paints contain oil which has been saponified by treatment with alkali, and therefore yield non-absorbent coatings. A drop of water splashed on to these may be wiped off without leaving any mark. A distempered surface, however, would be temporarily darkened. Water paints are particularly suitable for walls, as they are porous and allow the bricks to "breathe." At the same time they are impervious to water and thus offer a good protection to the walls.

* This table is taken from Friend's "Introduction, etc.," p. 148.

Whitewash and **Colour wash** are mixtures of lime and water, coloured in the latter case with cheap pigments. They are used in the interests of sanitation, rather than for decorative purposes.

Casein Paints.—It has long been known that the addition of casein (milk)* to lime washes increases their durability, the reason being that casein combines with lime to form agglutinant compounds which become insoluble on exposure to air. Casein is now largely added to certain paints, usually supplied in the form of powder by the manufacturer, containing casein and alkali in the dry state. When these paints are mixed with water the alkali is dissolved, and in turn dissolves the casein, which then reacts with the lime and colouring matters to form coloured cements. In casein paints the cementing substances usually consist of casein ("curds"), quicklime, and water, but sometimes the casein colours are mixed with linseed oil varnish. The paints must be kept hermetically sealed in tins. Only mineral colours can be used. The paints are manufactured by adding 200 parts of casein with 40 parts of powdered quicklime, and the colouring matter is added until a thick paste is obtained, the mass being then finely ground in a colour mill. Casein paints give extremely stable colours with a matte surface and are very cheap.

* See **Industrial Casein**, p. 79.

SECTION XVII

Textile Fibre, Bleaching, and Waterproofing Industries

TEXTILE FIBRE, BLEACHING, AND WATERPROOFING INDUSTRIES

By G. Martin, Ph.D., M.Sc.

PART I

INDUSTRIAL FIBRES

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See also under **Bleaching**, **Dyeing**, etc.

Two classes of fibres exist; (1) Vegetable, (2) Animal.

The former class consists essentially of cellulose (which see), while the latter consists of nitrogenous organic matter.

Vegetable Fibres

Cotton consists of thin, hair-like fibres enveloping the seeds contained in the capsule of the cotton plant, *Gossypium*. According to Royle and Kuhn four fundamental species exist, each comprising many varieties. The bulk of the cotton comes from the Southern States of the United States of America; perhaps the best cotton comes from *Egypt*; cotton plantations also exist in various parts of Africa, East Indies, and other tropical or semi-tropical regions.

The cotton filaments consist of long, thin cellulose cells 1·5 cm. long and 0.04 mm. in diameter, forming flat, ribbon-like bands, twisted spirally and hollow internally. They may be likened to tubes which have collapsed in the interior, thus acquiring a dumb-bell-like section. This hollow twisted construction makes fabrics constructed of cotton both light and elastic.

The cotton fibres when freshly separated in special machines from the cotton seed consist principally of cellulose (91 per cent.), but are surrounded by a thin cuticle, and contain about 5 per cent. of non-cellulose constituents, such as resin, colouring matter, proteids, fats, etc., which are almost completely removed during the bleaching process. Commercial varieties contain about 8 per cent. of moisture. Dilute alkalis (under 10 per

Fig. 199.—Cotton Fibres, Enlarged.

cent.) scarcely affect cotton fibres, but more concentrated alkali solutions "mercerise" them. (See **Mercerisation**, p. 205.)

Both bleaching and mercerisation increase the affinity of the fibre for colouring matter.

Dilute acids in the cold also do not attack cotton fibres, but when warmed or evaporated to dryness with dilute acids the fibres fall to pieces owing to the formation of hydrocellulose (which see). Use is made of this fact in obtaining **shoddy wool** (p. 517). Wool, silk, and other animal fibres have a much greater attraction for dyestuffs than cotton. To remedy this, cotton is often "animalised" by treating with **casein** or other nitrogenous matter (*e.g.*, milk + sodium stannate, then alum). Vignon and Cassella let $CaCl_2 + NH_3$ act on cotton at 60° C. Ammonia is absorbed, and the fibres can be dyed in an acid bath without a mordant.

Prior to being woven into fabrics cotton yarns are "sized" (to render them softer, more pliable, and adhesive) by dipping into flour paste, dextrine, gum, or other adhesive, and adding kaolin, $BaSO_4$, etc. etc., as weighting agents. (See p. 561. See also **Mercerisation**, p. 205.)

FIG. 199*a*.
Linen Fibres, Enlarged.

Linen consists of fibres of the inner bark or bast of the **Flax** plant, *Linum usitatissimum*, largely cultivated in North Ireland, Belgium, and Russia. The plants are cut, freed from seed, and then, in order to separate the bast fibres from the ligneous portion, they are "retted," *i.e.*, allowed to ferment in stagnant water contained in tanks. The woody tissues rot and the fibres are separated from them by beating, shaking, and other mechanical treatment. The fibres thus obtained are hollow, thick-walled tubes possessing a smooth polished surface tapering to a point at the end; they are 20-120 cm. long and 0.012-0.025 cm. broad. Linen fibres are stronger but not so elastic as cotton filaments; they are also better conductors of heat, thus explaining the cold feel attached to linen goods. Linen behaves with chemicals very similar to cotton; it is somewhat more inert to colouring matter and more easily disintegrated and injured by bleaching and oxidising agents than cotton; it contains 7-8 per cent. of moisture

Hemp is a fibre similar to flax, and is prepared in the same way from the hemp plant, *Cannabis sativa*. It contains more woody tissue than flax.

Jute is the bast fibre from several species of *Corchorus* (East Indies, India). The cut plants are 10-12 ft. in height and are made into fibre by retting. **Jute** consists principally of a compound of a tannic acid and cellulose which is called "bastose" and which is hydrolysed into its constituents by acids. Jute dyes with basic dyes much like wool.

Ramie is the fibre of China grass, belonging to the *Urticaceæ* or nettle family.

Cocoa-nut Fibre (Coir) consists of the fibrous layer covering the shell of the fruit of the cocoa-nut palm, *Cocos nucifera*, which is cultivated in most tropical lands. It is used for cordage, and as a filling and spinning material.

Sisal Hemp or **Agave Fibre** is indigenous to Yucatan, and is largely grown in the Bahamas and in Florida. The leaves of the plant average 5-6 ft. in length, and are cut when four years old.

New Zealand Hemp, or *Phormium tenax*, resembles Manila, but is inferior in strength and quality.

Manila Hemp is obtained from the leaves of a plant of the banana family, and is largely cultivated in the Philippine Islands, Borneo, and Java.

Esparto is a grass, *Stipa tenacissima*, growing in Spain, Algeria, and Northern Africa. Much used for paper making, etc.

Istle or **Tampico Fibre** is made from a plant largely grown in Mexico, and used in very large quantities in the United States.

Animal Fibres

Wool consists of the cleansed fibres of the sheep. The fibres vary in length from 2-25 cm., the shorter fibred varieties being termed "short stapled," "short wool," or "noils," and the longer ones, "long stapled," "long wool," or "tops." Long wools are manufactured into **worsted yarns**, while short wools go to make **woollen** or **carded yarns**. **Pulled wool** is separated from the skins of slaughtered sheep after a preliminary treatment with lime (which makes them difficult to dye). The fibres consist of a number of individual cells closely cemented together and overlapping so as to form a cylindrical solid curly fibre, covered with horny scales, which make the fibre look rough and uneven under the microscope.

FIG. 199*b*. Wool Fibre, Magnified.

The best and most expensive wool is given by the **Merino** sheep; wool is principally obtained from Australia, South America, and Africa; the crude wool as imported contains much sweat and fatty matter, which is extracted by washing, and gives the fat known as **Lanoline** (see pp. 53 and 60).

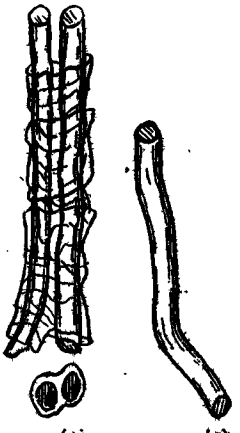
Wool consists of a substance called "keratine," which contains nitrogen (17.8-19.1 per cent.), sulphur (2.3-3.8 per cent.), carbon (49.8-52 per cent.), hydrogen (6.9-7.2 per cent.), and oxygen (20-21 per cent.). Boiling water causes the fibres to shrink up and mat together; warm alkalis decompose it, dissolving it to form fatty acids, amino acids, ammonium compounds, and sulphuretted hydrogen; weak bases, however, like ammonia, neutral soaps, and dilute acids, do not attack wool to any great extent. Bleaching powder, however, unless very carefully used, is liable to damage the fibre.

Shoddy Wool.—This consists of wool fibres recovered from old clothes and similar materials by a process known as "**carbonisation.**" The old cloth is soaked in a dilute solution of dilute HCl, $AlCl_3$, or $MgCl_2$, separated from excess of liquor by centrifuging, and then is heated to 100°-125° C. The cloth consists of a mixture of vegetable and animal fibres; when heated the cellulose forming the vegetable fibres is attacked by the acid, forming the brittle hydrocellulose. On beating the cloth the vegetable fibres fall to dust and are thus easily separated from the interwoven woollen fibres which remain intact—wool not being very sensitive to acids.

Among other industrially important fibres chemically similar to sheep wool but smoother and less curly may be mentioned: **Alpaca** from the South American goat, *Auchenia paco*; **Vicuna** from the small South American goat, *Auchenia vicugna*; **Mohair** or **Angora** from the Angora goat; **Cashmere** or **Tibet wool** from the Cashmere goat, **Llama hair** from the *Auchenia llama*; **Camel hair, Cow hair, Horse hair, Goat hair**, etc.

Silk is the cocoon thread of the silk spinner, *Bombyx mori*, which is widely cultivated on mulberry trees in China, Japan, France, Italy, India, Asia Minor, etc. The spinning glands of the mulberry silkworm secrete two colourless liquids, which unite on issuing from the glands to form the yellowish double-thread known as silk. The worm winds the fibre around itself as an enveloping cocoon of length 400-1,300

yds., before passing into the chrysalis or pupil state. The chrysalis is killed by dry heat, steam at 75° C., or by freezing, and the cocoons are then immersed in hot water to soften the silk glue known as **sericin** which forms the exterior layer of the filaments, and binds the strands together. The silk threads are then twisted on a reel to form the threads of **raw silk**. Only 50-66 per cent. of the silk in the cocoon can be reeled. The waste parts of the cocoon yield (after boiling with soda solution, combing, and spinning) the so-called "**floss silk**," which is made into **spun silk**. The waste from the spinning is sold as **silk wadding**.



Double Silk Threadshowing Cementing Envelope and Section. Degummed Silk Fibre.

FIG. 199.—Silk Fibres.

Raw silk fibre consists of about 66 per cent. **fibroin**, $C_{15}H_{23}N_5O_6$, forming the real silk substance, and the silk gum or **sericin**, forming the exterior layers. To make the silk bright and lustrous the gum must be removed from the fibre by treating with hot, neutral soap solution, the strands being then washed with dilute sodium carbonate solution. The soap baths containing the dissolved gum are called "boiled-off baths," and are used in silk dyeing. Degummed silk is called "Cuite"; it is very lustrous and soft, but has lost 20-30 per cent. of its original weight. The "rustling" property of silk is attained by further treatment of the cuite in an acid bath. If the degummed silk is not to be dyed dark it is "boiled white" by sewing into coarse sacks, boiling with soap solution for thirty minutes, washing with Na_2CO_3 solution and H_2O, bleaching with H_2O_2 or SO_2, and again washing. Silk substance—both the sericin and fibroin—is rapidly dissolved by alkalis, zinc chloride, and cuprammonium; dilute acids do not attack it so readily. Silk is very hygroscopic, containing on an average 11 per cent. of water, and capable of absorbing nearly 30 per cent. without appearing damp. Consequently the estimation of the water is of great importance in the silk trade, and is carried out in "conditioning" apparatus.

Several varieties of **Wild silks** are known, the most used being Tussore silk or Tasar silk, spun by the *Antheræa mylitta*, of a bright brown colour, very durable, and having a fibre thicker than that of genuine silk. Many of the wild silks are very difficult to properly bleach and dye.

For **Artificial Silk** see p. 219.

Statistics.—The following figures show the enormous value of the *import* of textile fibres into the United Kingdom:—

	Imported in 1910.	Value.
	Tons.	
Raw cotton, yarn, and waste	903,000	£72,760,000
Linen yarn	14,400	1,050,000
Coir fibre and yarn	3,200	250,000
Hemp (also tow and yarn)	733,000	3,280,000
Jute (also yarn)	298,000	4,720,000
Silk (including yarns, waste, etc.)	4,900	1,880,000
Wool (including yarn, shoddy, and rags)	500,000	40,120,000
		£124,060,000

The corresponding statistics for imports into the United States are :—

	Imported in 1910.	Value.
	Tons.	
Cotton (unmanufactured, waste and yarns)	58,300	$21,710,000
Flax	12,761	3,536,000
Hemp	6,423	1,040,000
Istle or tampico fibre	9,272	645,000
Jute	68,155	3,728,000
Manila	93,253	10,517,000
New Zealand flax	3,353	363,000
Sisal grass	99,966	11,440,000
Alt other grass	12,248	1,148,000
Coir yarn	2,720	204,000
Human hair	....	2,848,000
Horse hair	2,410	2,107,000
Other animal hair	5,960	1,065,000
Wool, camel hair, goat hair (unmanufactured)	117,800	51,220,000
Silk (cocoons, raw, waste)	10,470	67,129,000

The United States exports were :—

	Exported in 1910.	Value.
	Tons.	
Cotton (unmanufactured)	1,431,600	$450,447,000
Hair	...	1,143,000
Silk waste	1,200	64,000

PART II

THE BLEACHING OF TEXTILE FIBRES

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Textile fibres, either as yarn or woven into cloth, must undergo several preliminary operations before they can be passed on to the dyer and printer. By the process of "bleaching" heterogeneous matter in the fibre is largely destroyed or removed so that the cloth dyes equally in all parts.

Linen bleaching is usually carried out by spreading the material on meadows in bright sunshine, keeping the material well sprinkled with water. The sunlight causes the formation of hydrogen peroxide or ozone, which oxidises the lignin. As a result the linen acquires the snow-white colour so characteristic of it.

Cotton is nearly always bleached by chemicals, usually by treating with caustic soda and calcium hypochlorite (bleaching powder) or sodium hypochlorite (prepared by the electrolytic process) solution. The caustic soda attacks the lignin and saponifies fats, dissolves resins, etc., while the hypochlorite completes the process by its strong oxidising action:—$HClO = HCl + O$.

The cotton goods are sewn together in special machines so as to make a roll about $\frac{3}{4}$-$1\frac{1}{4}$ yds. wide and sometimes 50,000 yds. long, and are then usually made to undergo the following series of operations:—

(1) *Singeing.*—They are passed through a singeing machine (Fig. 200) in which a gas flame plays on the cloth whereby the finer projecting fibres are burnt off. If

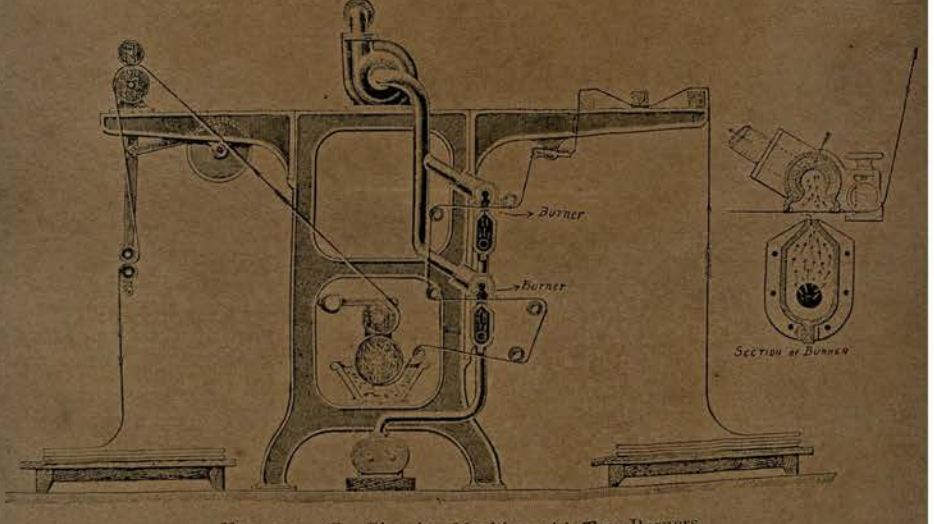

FIG. 200.—Gas Singeing Machine with Two Burners.
(Mather & Platt, Manchester.)

allowed to remain on these fine fibres would cause a smearing of the colours in printing.

(2) *Steeping or Souring.*—From the singeing room the goods are drawn in rope form through a porcelain ring ("pot's-eye"), and are treated with very dilute H_2SO_4 in a *souring machine* (Fig. 201).

This consists of a tank filled with the acid solution and provided with wooden rollers; the hanks pass through porcelain rings (pot's-eye) into the acid bath, thence coming out, are squeezed free from liquor in a roller, and then pass again into the liquor, and are squeezed dry again, the process being

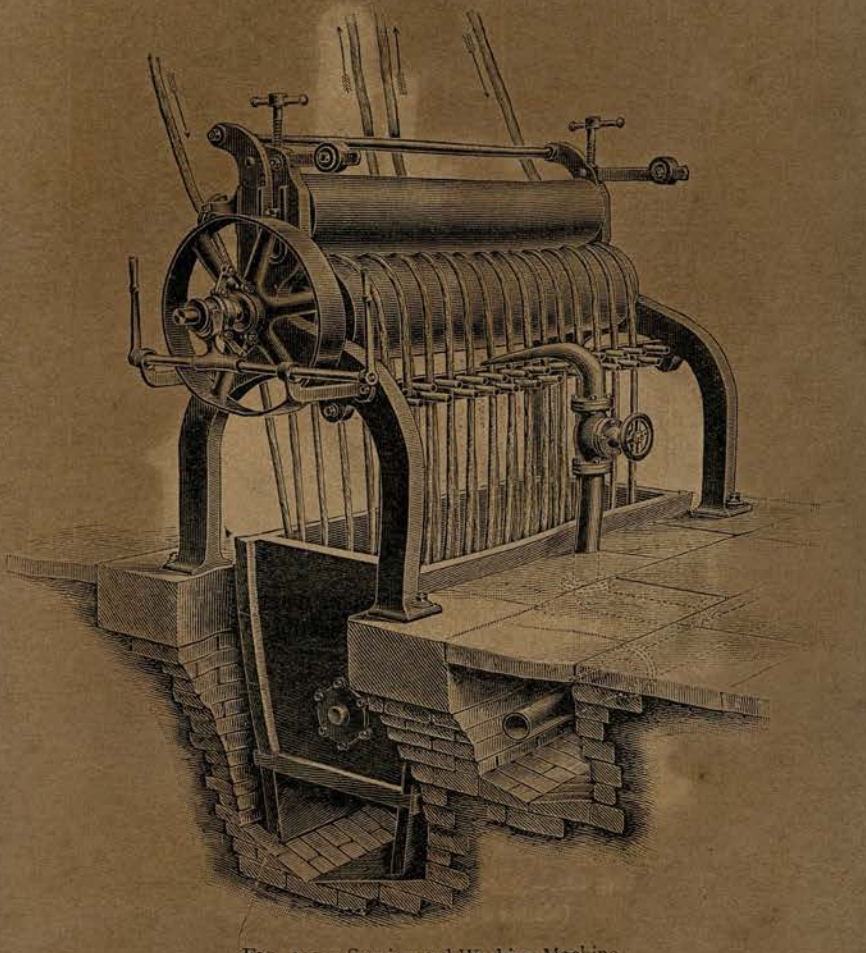

FIG. 201.—Souring and Washing Machine.
(Mather & Platt, Manchester.)

repeated several times. After about twenty-four hours the acid completely hydrolyses all starch used for sizing the cotton and at the same time dissolves mineral impurities.

(3) The goods are then washed free from acid and mineral salts ("filling") in another similar machine. (4) The goods are next heated under pressure with dilute (3 per cent.) caustic soda in the autoclave—called a "Keir" ("bowking").

A diagram of Mather & Platt's apparatus is shown (Figs. 202 and 203). The goods soaked in caustic soda solution are placed in a perforated truck and run into the horizontal boiler (which is

capable of holding 1,270-3,400 kg. of goods) and the door mechanically shut. By means of an injection apparatus and centrifugal pump boiling caustic soda is forced in at the bottom, and caused to continually circulate through the goods, the heating being carried up to 2½ atmospheres for some hours, and being caused either by live steam coils placed in the bottom of the boiler, or by closed heating coils containing hot air or steam coming from an external source of heat. While one truck of goods is being treated the men are loading another truck externally, so that charging and recharging the apparatus takes little time. When the 3 per cent. caustic soda solution is pumped in at the bottom, all the air is driven out by steam. Unless all the atmospheric oxygen has been removed from the boiler the cloth may become rotten probably owing to the formation of oxycellulose. Vertical high pressure keirs are also used. Fig. 204 shows Farmer's high pressure kier.

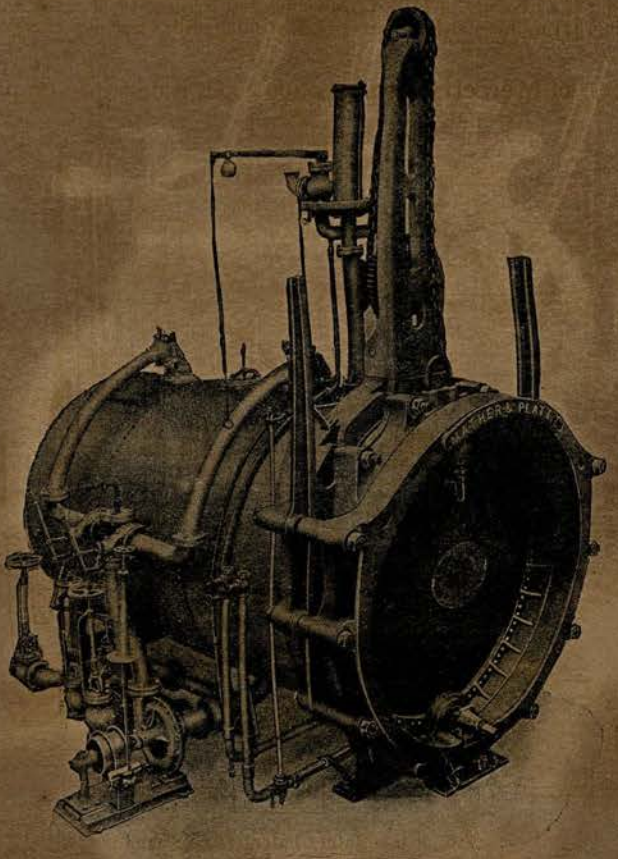

FIG. 202.—Mather Patent Keir (Full View).
(Mather & Platt, Manchester.)

The goods are now almost white. After cooling they are (5) washed free from caustic soda, and then (6) *bleached* in large tanks with a dilute solution of bleaching powder (1 g. bleaching powder to 1,000 c.c. water). No acid is used, the goods being allowed to remain in the bleaching liquor for some time ("chemicing"). (7) Next the goods are washed, and the excess of chlorine and calcium salts removed by passing (8) through dilute acid followed by (9) a thorough washing.

(10) The cloth is now dried by passing over a series of steam-heated hollow copper rollers; (11) again passed through singeing machines to remove fine projecting fibres; (12) well beaten, and (13) rolled up, whence it goes to the dyers or cloth printers.

The succession of operations is often varied widely according to the goods and the purpose for which they are intended. Thus pieces to be dyed dark colours require a different treatment to those intended for lighter shades or white finishes.

Thus many firms work by the process of *double bowking*, viz., by boiling with lime first and soda or resin lye after, or by means of a strong caustic lye alone (*single bowking*). The souring and "chemicing" (*i.e.*, treating with bleaching chemicals) is done either in souring or "chemic" cisterns arranged with circulating pumps, or by thoroughly impregnating or saturating the goods in souring or chemicing machines, and then letting them stand in heaps for some time. The latter method is simplest and is most widely used in England at the present time, whereas the former possesses the advantage of putting less strain on the goods.

Many firms adopt the following series of operations: (1) Singeing, (2) liming and filling in lime keir, (3) bowking (*i.e.*, boiling in keir), (4) washing and souring, (5) washing and filling in soda keir, (6) bowking, (7) washing and chemicing (*i.e.*, treating with bleaching chemicals), (8) souring, washing, and *squeezing off*.

The process of **Mercerisation** of cotton goods is described on p. 205.

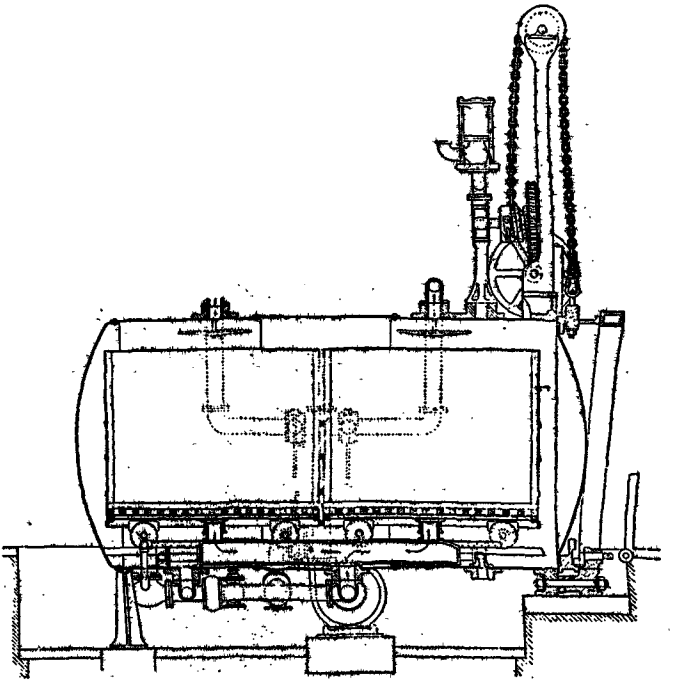

Fig. 203.—Mather Patent Kier (Section).
(Mather & Platt, Manchester.)

Bleaching of Wool.—Before subjecting to the bleaching chemicals all oil (used in spinning the wool) is carefully removed by washing with ammonium carbonate, soda, or soap: soft water must be used for the purpose. The wool is then bleached either by treating with a bisulphite solution or by exposing it moist to the fumes (SO_2) of burning sulphur. For the latter purpose sulphur—about 8 per cent. of the weight of the wool to be treated—is burnt in closed chambers in which the wool is suspended.

A very good white is obtained by bleaching with **Hydrogen peroxide**, H_2O_2; a dilute solution is made weakly alkaline with ammonia and the wool immersed until white. (Hydrogen peroxide is also used for bleaching silk, ivory, hair, etc.). **Sodium peroxide**, Na_2O_2, has also been used. This thrown into water decomposes, yielding oxygen and caustic soda. The oxygen bleaches the wool, although much available oxygen escapes unutilised in the free state. Since the caustic soda produced

attacks the wool, magnesium sulphate (Glauber's salt) is added to destroy its corrosive effect. The sodium peroxide process is neither so easy nor certain as the hydrogen peroxide or sulphite process.

Sometimes before the wool is finally passed on to the dyer and printer it is

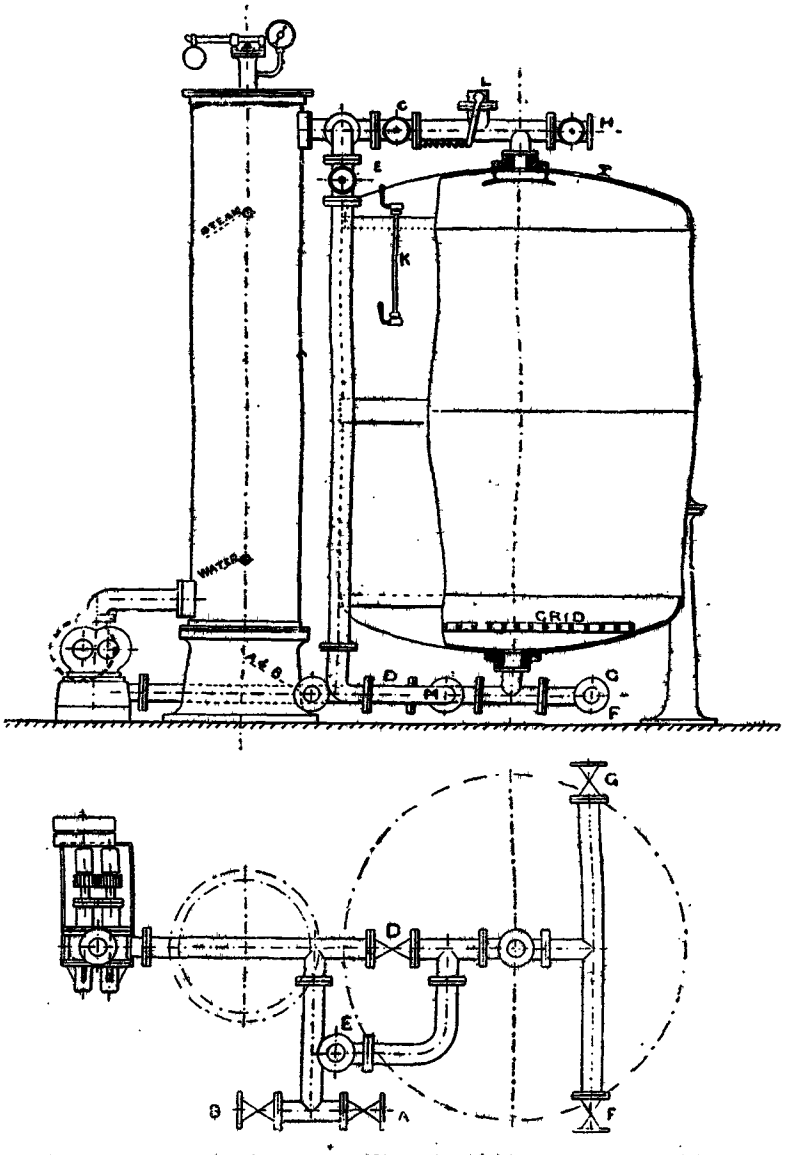

FIG. 204.—Farmer's High Pressure Kier, with Multitubular Heater and Pump. (Sir James Farmer & Sons Ltd., Manchester.)

subjected to a very weak bleaching powder solution, mordanted with sodium stannate ("Tin salt"), and then treated with dilute sulphuric acid. Wool treated thus dyes very well.

Silk Bleaching.—After "degumming" (see **Silk**, p. 517) by warming with

neutral soap solution and then (if the silk has to be dyed a light shade) by "white boiling" (see p. 518), the silk may be directly transferred to the dye bath; the "boiled-off baths" containing the silk gum dissolved in the soap solution used for degumming are used in the dye baths. Occasionally silk is bleached with hydrogen peroxide or sulphur dioxide, and, indeed, **wild silks** must be bleached with hydrogen peroxide. Modern silks are strongly "weighted" with tin chloride, water-glass, and sodium phosphate, the weight being sometimes doubled thereby without injury to the lustre or dyeing power of the silk. However, such weighted silk is far less strong and durable than the pure silk; indeed it is scarcely better in these respects than artificial silk. When the silk is to be dyed a dark shade, such weighting and colouring agents as tannic acid and potassium ferrocyanide, iron sulphate, etc., may be used.

PART III

WATERPROOFING AND MAKING NON-INFLAMMABLE OF TEXTILE FABRICS

LITERATURE

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ANDÉS.—"Feuersicher-, Geruchlos- und Wasserdichtmachen." Vienna, 1896.
EISENSTEIN.—*Allg. Chem.-Ztg.*, 1905, p. 507.

Several distinct methods of rendering fabrics waterproof are practised:—

Waterproofing with Aluminium Acetate.—The fabric is impregnated with a dilute solution, 5° Bé., of aluminium acetate (which is often prepared by the waterproofer himself by treating alum or aluminium sulphate with calcium acetate or lead acetate), dried in hot air, and drawn through a 5 per cent. soap solution. Insoluble aluminium soaps are precipitated on the fibre and render the material waterproof:—

Aluminium acetate + Sodium soap ⟶ Aluminium soap + Sodium acetate.

A trace of undecomposed soap remains in the fabric; this, after drying, would give the fabric a soft slippery feel; it is therefore removed by passing the soaped fabric through a solution of alum or aluminium acetate, rinsing and drying.

Impregnating the fabric with aluminium acetate and completely drying at a steam heat will render the fabric fairly waterproof owing to the formation of insoluble aluminium compounds in the fibre. Sometimes this alone is done; sometimes the fabric is, after drying, passed through an alum solution in order to render the fabric more completely waterproof. India-rubber, paraffin, etc., is introduced into the soap solution (soap solutions form emulsions with fused waxes and paraffin, petroleum, rubber solutions, etc.). Japan or Carnauba wax is often used. The rubber is dissolved in paraffin, linseed oil, and palm oil.

The Badische Anilin- und Soda-Fabrik recommend the two following processes for waterproofing dyed cotton or linen material:—

(1) Soak the dyed pieces in a solution of 5 lbs. soap in 100 gals. water, squeeze, pass through a solution of 10 lbs. alum in 100 gals. water; squeeze and dry. Repeat whole process if necessary.

(2) Prepare a soap emulsion by boiling together 6 lbs. white soap, 3 lbs. tallow, 3 lbs. stearine. Pass the dry pieces through the emulsion at 70°-85° F., squeeze, and pass through a cold solution of aluminium acetate of 5° Tw. Rinse lightly and dry hot.

It should be noticed that by this method the interstices between the threads are not filled up, the fibres keeping the water back mechanically. In true waterproofing this should always be the case.

According to German Patent 141,411, fabrics are waterproofed without destroying their porous nature by impregnating with aluminium acetate, drying, and impregnating with lanoline or wool-fat dissolved in volatile solvent.

Waterproofing with Paraffin.—The materials are passed through a dilute solution of paraffin, ceresine, or similar body, dissolved in light petroleum or other volatile solvent. The solution fills the cells of the fabric and the solid matter is left behind when the solvent evaporates.

Sometimes the ceresine, paraffin, etc., is applied in a *melting* state by means of rotating a metallic roller in contact with the solid hydrocarbon, so that it carries away portions of it and puts them on the fabric, which passes between the roller and a heated trough; the latter fuses the hydrocarbons so that they are soaked up by the fabric as fast as they are fused. The goods are finally calendered.

Waterproofing with Gelatine, Tannin, Caseinate of Lime, Chrome Gelatine.—The materials are treated with glue or gelatine and afterwards with tannin or alum which renders the gelatine insoluble (see **Gelatine**).

Cotton goods are often treated with 1.5 kg. of gelatine in 50 l. of boiling water containing 1.5 kg. soap chips, 2.5 kg. alum. The cotton is put through the solution at 50° C., dried, and calendered. Cellulose materials are often waterproofed by impregnating with a solution of 1 part gelatine, 1 part glycerol, 1 part tannin in 12 parts water.

Sails, carriage aprons, tarpaulins, etc., are often saturated with gelatine solution (7 per cent.) at 40° C., air dried, passed through a 4 per cent. alum solution, air dried, rinsed, dried. Sometimes the materials are impregnated with chrome gelatine, which is rendered insoluble by exposing the material to light. A well-known recipe consists in dissolving 5 parts gelatine, 1 part potassium bichromate, and 1 part of acetic acid in 30-50 parts of water, adding 5 parts of cuprammonium (ammoniacal solution of copper oxide), brushing the material on the fibre, and drying in air.

Casein waterproofing is carried out by stirring it into a cream with water, and adding 2.5 per cent. its weight of slaked lime; then dissolving casein in alkali solution, mixing the solutions, impregnating the fabric with the mixture, and passing it through aluminium acetate solution, which precipitates an insoluble aluminium caseinate.

Waterproofing with Cuprammonium, Viscose, and other solvents for cellulose. The celebrated Willesden fabrics are made this way by cuprammonium. For details see under **Cellulose**, pp. 189, 213.

Waterproofing with Solutions of Caoutchouc.—See under **India-rubber**, p. 360.

Waterproof Oiled Fabrics are made by spreading over the material in several successive layers a paste consisting of half-raw and half-boiled linseed oil, mixed with mineral colouring matter. The material is dried between the successive applications. Siccatives, resin, petroleum, etc., are sometimes added. For **Oil Cloth** and **Linoleum** see p. 49.

Tarpaulins are made by painting suitable fabrics with tar which has been heated to drive off the more volatile oils (but under 300° C., otherwise the tar becomes unsuitable).

Manufacture of Non-Inflammable Fabrics.—Clothes and fabrics may be made almost uninflammable by soaking in a solution of alum, ammonium phosphate, borax, water-glass, and similar chemicals. Sodium tungstate has been used for making ball dresses non-inflammable; borax and alum, borax and magnesium sulphate, gypsum and ammonium sulphate are all good mixtures. Water-glass makes the material stiff. Ammonium phosphate leaves the material soft. A full account is given in Andés' book, "Feuersicher-, Geruchlos- und Wasserdichtmachen" (above).

W. H. Perkin's method of *permanently fireproofing cotton goods* (*e.g.*, "non-flam." flannelette) is this:—The flannelette is impregnated with a solution of sodium stannate of about 45° Tw., squeezed, dried on heating copper drums, passed through ammonium sulphate solution of 15° Tw. (in order to precipitate tin oxide), squeezed, dried, washed to remove Na_2SO_4, dried and finished in the usual manner. The treated material can be dyed the most delicate shades, has no poisonous action on the skin, and is stronger and more durable than the untreated material. The cost is not more than 1d. per yard with tin at £210 per ton. Muslin curtains can be treated similarly (see *W. H. Perkin, Eighth Int. Cong. Appl. Chem.*, New York, 1912). Also Patents—French Patent, 321,063 of 1902; English Patents, 8,509, 1902; 24,222, 1903.

Statistics.—England exported in 1910 waterproofed apparel to the value of £499,000, and imported £7,000 worth.

SECTION XVIII

Dyeing and Colour Printing Industry

DYEING AND COLOUR PRINTING INDUSTRY

By Henry J. S. Sand, D.Sc., Ph.D.

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INTRODUCTION

The object of the dyer of textiles may be said to be to impart to them, by treatment with certain solutions, a uniform colour which should be as permanent as possible to solvents and other influences. The methods of obtaining this end are manifold, and it is not to be supposed that any one explanation will fully cover all the processes employed. Even where the operations carried out in various cases are apparently similar or identical, the theory underlying them may be entirely different.

The simplest classification of dyestuffs is that, into those which are taken out of solution directly by the fibre, and into those which are produced chemically as insoluble substances during successive operations of dyeing. The former are usually termed "**substantive**," the latter "**adjective**" dyes. Dyestuffs like indigo which are reproduced in the fibre in their original condition, during successive operations, are usually said to belong to the former class, although, according to the definition just given, they would more correctly be considered to be members of the latter. Another classification often employed is that into "direct" dyes, *i.e.*, practically the same as substantive dyes and "**mordant**" dyes, *i.e.*, such as can only be applied with the intervention of a mordant. Lastly, dyes are sometimes spoken of as "**monogenetic**" when they will yield only one colour whether applied directly or with the aid of different mordants, and as "**polygenetic**" when they will yield different colours according to the mordant employed.

Substantive or Direct Dyes.—If a piece of silk, wool, and cotton be each boiled with the solution of a basic dye, such as Victoria blue or the acidified solution of an acid dye, such as acid magenta, it will be found that the silk and the wool have been dyed, whereas the cotton will probably only have acquired a slight stain which may be easily removed by washing. If the solution of the dyestuff be fairly dilute the animal fibre will remove all of it, leaving a colourless liquid behind. Again, when wool or silk is dyed with the hydrochloride of a basic dye, such as magenta (rosaniline hydrochloride), it has been shown by Knecht and Appleyard

that the whole of the hydrochloric acid is left in solution and the fibre is dyed red, in spite of the fact that the base which alone has been removed from solution is colourless. Indeed it was shown by Jacquemin as early as 1876 that when either wool or silk is boiled with a colourless solution of rosaniline base, it is dyed red. These facts all point to the conclusion that the dyeing of animal fibres with most of the basic dyes is a process of a more or less chemical nature, consisting of the combination of some substance contained in the fibre with the base of the dye. Experiments may also be adduced to show that the dyeing of animal fibres with the majority of acid dyestuffs is a similar process, a conclusion which need not surprise us, for we have every reason to believe that not only wool and silk, but also most of the substances which may be formed from them by chemical decomposition, are of the nature of amido acids, *i.e.*, they have the properties both of acids and bases, and will, therefore, readily combine with dyestuffs having basic or acid properties.

The following facts may further be adduced to confirm the conclusion that acid and basic dyestuffs are usually held by the animal fibres in a very firm manner approaching that of chemical combination. It has been shown by Dreaper in numerous cases that, when held by the animal fibre, a dyestuff is much less readily acted upon chemically than when it is in combination with a vegetable fibre, such as cotton, or than when it is in the free state. Thus, the direct cotton dye primuline was dyed on samples of silk and cotton and then diazotised. In the former case the resulting compound was shown to be incapable of coupling with R salt, whereas in the latter combination instantly took place just as if the diazotised dye had been in the free state. Similarly, the acid dye methyl orange is not turned red so readily by acid when on silk as when in solution, which points to the conclusion that it forms an orange compound with the silk. Then again, it has been shown by Knecht that the laws which govern chemical combination are to some extent obeyed; for when different acid colouring matters of similar composition were employed in the dyeing of wool in strong solution and under similar conditions, the quantities taken up by the fibre stood in the ratio of their molecular weights.

The action on the fibre during the process of dyeing of substances other than the dyestuff is probably of the very greatest importance. Thus it appears that two slightly soluble substances which have been named respectively lanuginic and sericinic acid are produced by the action of hot water or acid on wool or silk, and it is these substances which combine with the basic or acid colouring matters of the bath. In fact it has been shown by Knecht that if wool is first boiled with 5-10 per cent. sulphuric acid, and then thoroughly washed, it dyes fuller shades in the neutral bath of acid colours than would be obtained in the ordinary way even if acid were added. This experiment is of great interest, for it shows that what is actually dyed by chemical combination is probably not the whole of the fibre, but mainly a constituent produced from it by the action of water during the operation of dyeing. Furthermore it opens up the probability that the chemical process takes place largely in solution, a chemical compound of lanuginic or sericinic acid with the dye being first produced in the liquid, and then absorbed by the fibre by one of the processes of solid solution or colloidal precipitation discussed in the sequence. The fact that many dyes may be extracted from wool and silk by alcohol is sometimes adduced as an argument against chemical combination, but what is extracted in this case may very possibly usually be the chemical compound of the dyestuff with lanuginic or sericinic acid, and not the dyestuff itself.

The dyeing of cotton is probably under all circumstances a process of a slightly different order from that usually taking place with the animal fibres. During the last twenty-five years a large number of direct cotton dyes has become known. When cotton is treated with the solution of any one of these substances, it will extract a considerable amount of dyestuff from solution, and thus become dyed; the remaining liquid will, however, be found to be by no means colourless but to retain a very large proportion of the dyestuff. Again, if the dyed fibre be treated with pure water a considerable proportion of the dye will be extracted, and by repeating the operation almost the whole may be withdrawn. The process of dyeing in this case is thus seen to be a "reversible" one, and may fairly be compared with what takes place when the solution of a substance soluble in water such as benzoic acid is shaken with a liquid such as ether in which it is likewise soluble. The solution in ether

which is thus obtained may be compared with the dyed fibres; and the latter may be termed a "solid solution" of dyestuff in the cotton.

The introduction of the idea of solid solution into the theory of dyeing is due to O. N. Witt, who, however, attempted primarily to apply it to animal fibres. A law which particularly characterises solution in contrast to chemical combination is that known as Nernst's distribution law. In its application to the dyeing of fibres this law demands that if a series of experiments is carried out in which given weights of the same fibre are dyed in a given volume of the solution of the same dyestuff, containing, however, different quantities of the latter in each experiment, then after equilibrium has been established, the expression $C_f : C_s^{\frac{1}{n}}$ should have the same value in each experiment. In this expression C_f indicates the amount of dyestuff taken up by the fibre, C_s the amount left in the solution, and n the ratio of the molecular weight of the dyestuff in solution and on the fibre respectively. It has been shown particularly by v. Georgievics that this relation does hold for the dyeing of cotton in many cases, and also in a few for the dyeing of wool and silk. It must be pointed out here, however, that a relation of similar form holds for the process of "adsorption" of colloids discussed in the sequence, and that experiments on distribution like those of v. Georgievics can, therefore, not distinguish between the phenomena of solution and adsorption.

Adjective Dyes.—In all cases where the dyestuff is produced as an insoluble substance by the interaction of two soluble ones in the interior of the fibre, the processes of chemical combination with the fibre and solid solution in it may play a part, but in addition we have the possibility of the solid being trapped by the cell walls in a purely mechanical manner, and also that it may be held by them by the phenomenon of adhesion. It must be pointed out here that there are no doubt continual gradations possible between purely mechanical processes, the physical phenomena of adhesion, adsorption, and solid solution, and finally the process of chemical combination; and very probably all these gradations occur in one or another of the manifold operations which are carried out in dyeing.

A physical phenomenon which no doubt plays an important part in many of the processes of dyeing is the formation of so-called "adsorption" compounds. This phenomenon, the importance of which in dyeing has been pointed out in particular by P. Zacharias, has recently led to a "colloid-compound" or "electrical" theory of dyeing.

A large number of substances of importance to the dyer, such as tannin, many dyestuffs, such as congo red, crystal violet (base), night blue base, etc., and the fibres themselves belong to the class of colloids. Many of these substances will dissolve in water, forming what are termed colloidal solutions, *i.e.*, solutions in which the dissolved particles are of a much larger order of magnitude than those of ordinary solutions, so that they will not diffuse through parchment and may usually be made visible by means of the ultramicroscope. These dissolved particles have been proved to bear electric charges, those of a basic nature acquiring a positive, those of an acid or neutral nature usually taking up a negative charge. It has also recently been shown by Gee and Harrison that all the fibres become negatively charged in contact with pure water, whereas in contact with acids they usually assume a positive charge. Now, if a colloidal solution containing positively charged particles is added to one in which negatively charged particles are present, these mutually attract each other and combine, to form what are called adsorption compounds. The latter are precipitated from solution, the electrical charges being neutralised at the same time. There can be little doubt that the "triple" compounds formed between tannin, metal oxides, and dyestuffs, on which the dyeing of basic dyes on cotton mainly depends, are largely due to colloidal combination, and this same phenomenon may probably play an important part in many other processes such as the fixation of metal oxides and other substances on the fibre.

Water

Most natural waters show an alkaline reaction, and for purposes of mordanting, dyeing with basic colours, and washing after dyeing should be carefully neutralised before use by a suitable acid. Sulphuric or acetic acid may be employed. The latter, though more expensive, is preferable, since a small excess accidentally added will usually not be harmful. When employing the former it may often be advantageous to add a small amount of sodium acetate in order to neutralise the free mineral acid.

For dyeing with acid colours, it will usually be indifferent whether the water employed is originally alkaline or not, since enough acid is always added during the process of dyeing to make the bath strongly acid. For dyeing with direct cotton dyes and sulphur colours hard waters should be softened before use.

Water containing even small quantities of iron or other heavy metals is as a rule useless for dyeing and mordanting operations, since the iron will usually combine with the dye, thus acting as a mordant, and produce a dull or "saddened" colour. The iron must, therefore, be got rid of by a process of softening. For use with acid dyes a very small amount of heavy metals will as a rule not be harmful. The presence of lime in large quantity in a water must be taken into consideration, since it will act as a mordant, and may often produce undesirable results. In some cases, such as in the dyeing of turkey red, the presence of lime is desirable, since it acts as an additional mordant, and produces better shades than would be otherwise obtained.

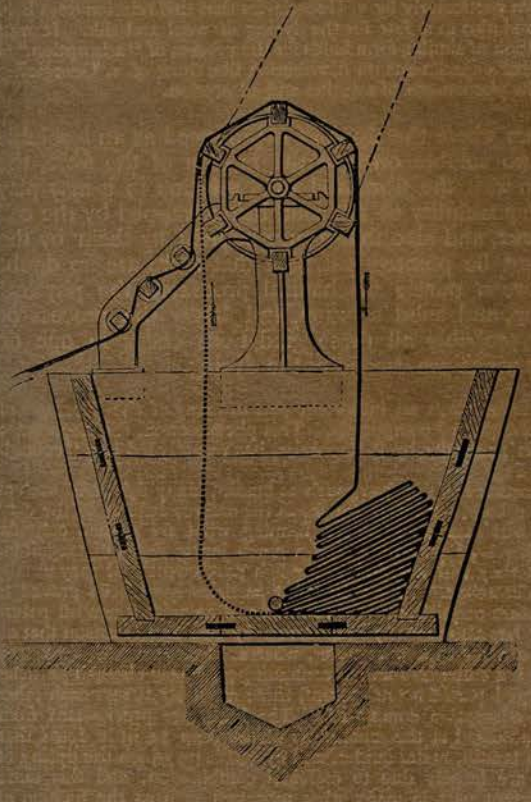


FIG. 205.—Dye Vat and Winch for Pile Fabrics.
(Mather & Platt, Manchester.)

Appliances and Machinery used in Dyeing

Preparation for Dyeing.—The material must be freed completely from all fatty impurities by the processes described in the chapters on bleaching before it comes into the dye bath, and this refers not only to such fats and waxes as are naturally present in the fibre, but also to those which are added artificially during the operations of spinning and weaving. Bleaching is usually only necessary when delicate or bright shades are to be dyed. Wool may be carbonised either before or after dyeing in order to remove vegetable impurities such as burrs, pieces of straw, etc. In almost all cases the fibre should be thoroughly wetted out before it comes in contact with the dyeing liquid.

Dissolving the Colours.—All dyestuffs and pastes should be dissolved in condensed water and preferably filtered through cotton cloth before they are added to the dye bath. Dyewoods may be extracted in the dye vats at boiling temperature before entering the goods. For this purpose the chips are placed in bags and preferably extracted systematically, *i.e.*, the fresh chips should be employed to bring the bath completely up to strength, whereas the almost exhausted wood should be completely extracted in a bath containing fresh water. Special extractors, apart from the dye vats, are also frequently employed, and devices are also in use which may be fitted to the dye baths and in which the wood may be continuously extracted while the latter are in use.

All dyeing machinery may be said to consist of an arrangement for either moving the goods through the more or less stationary dye liquor, or for causing the dye liquor to circulate through the stationary goods. In addition, an arrangement for heating the dye vat, usually either by steam pipes or by live steam, is provided. At the present day the textile fibres are dyed in practically all stages of manufacture; the

FIG. 206.—Double-Walled Copper Dye Vat.
(Mather & Platt, Manchester.)

dyeing of the finished cloth, or piece-dyeing, however, still transcends in importance that of the other partially finished forms.

Dyeing of Piece-goods.—The simplest form of machine and the one most usually employed for woollen cloth consists of the dye vat and winch.

Fig. 205 shows an arrangement of this kind in which a wooden dye vat is employed. The pieces are stitched together before dyeing and are usually run as an endless band over the winch. The

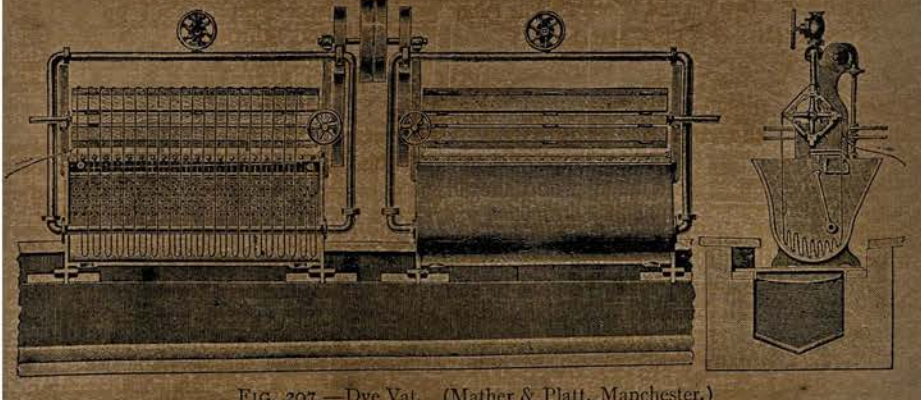


FIG. 207.—Dye Vat. (Mather & Platt, Manchester.)

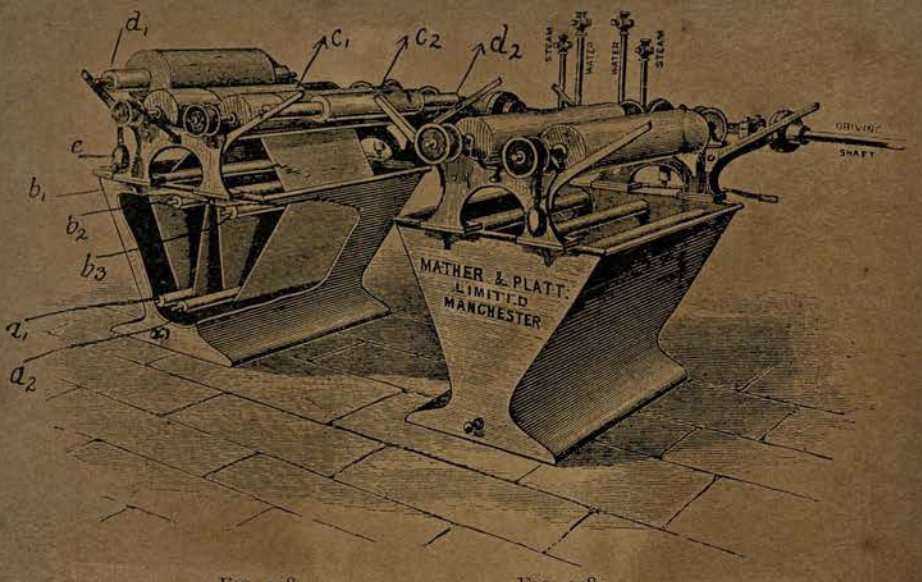


FIG. 208. FIG. 208*a*.

Dyeing Jiggers. (Mather & Platt, Manchester.)

latter may be turned by machinery or by hand. The dye bath is usually heated by direct steam issuing from a perforated pipe. Fig. 206 shows a double-walled copper vat which is heated by steam introduced between the two copper walls. In this vat the steam does not mix with the dye liquor, and dilution of the latter is thus avoided during dyeing. Fig. 207 illustrates a vat in which the pieces in rope form are drawn as an endless band in a spiral over the same winch a large number of times after remaining in the liquid for a short time. Guide pegs prevent them from becoming entangled.

The machine most frequently met with in the dyeing of cotton cloth is the jigger. In this machine the cloth in full width is passed through the dye liquor several times over guide rollers.

In Fig. 208 two of these rollers, a_1, a_2, are shown submerged in the liquid, and three, b_1 b_2, b_3, are placed above. In addition, two draw rollers, c_1, c_2, and two batch rollers, d_1 and d_2, are visible above the vat. The cloth is first run from c_1 to c_2, the roller c_2 being actuated directly by the driving machinery, while the brake c is placed on c_1. The cloth is thus kept in a state of tension. When all the cloth has been run on to c_2, the motion is reversed, c_1 being made the driving roller, and the brake being put on c_2. This alternate motion is continued until the piece has been dyed the desired shade. The pipes necessary for the supply of water and steam for heating are indicated in Fig. 12*a*.

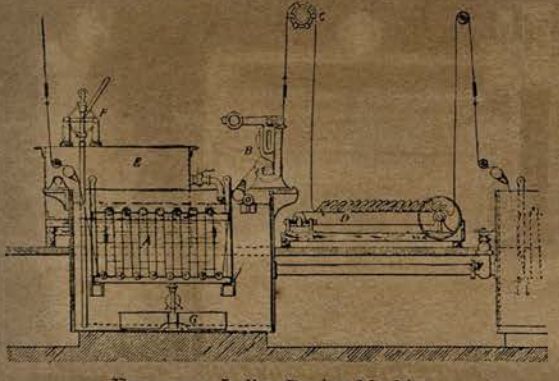


FIG. 209.—Indigo Dyeing Machine.
(Mather & Platt, Manchester.)

For **indigo dyeing**, pp. 461 and 554, vats are employed in which the cloth is run over a large series of rollers completely submerged in the liquor. It then passes through squeezing rollers, and over a series of rollers placed in the air above the vat for the purpose of oxidising the leuco compound absorbed by the fibre. Another arrangement shown in Fig. 209 for the purpose of oxidising the leuco compound, consists in piling the cloth loosely on an endless travelling band. The dye vat must be supplied with a stirring arrangement G, which can be actuated at will when the vat is being freshened up. Several vats of increasing strength are usually

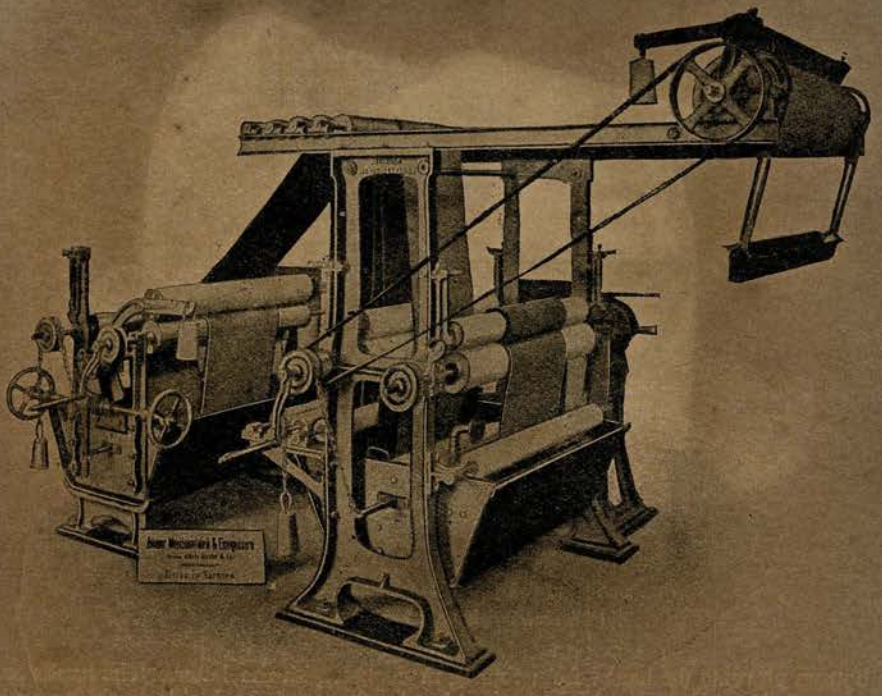


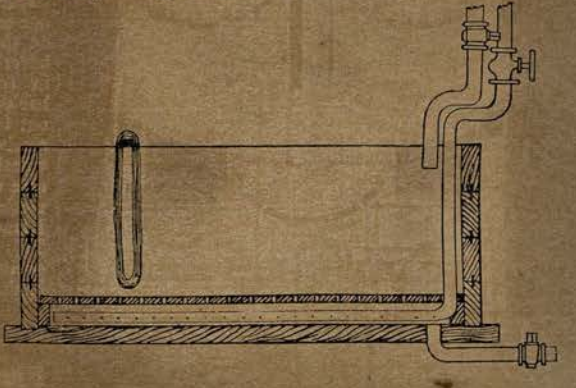
FIG. 210.—Jiggers for Sulphur Blue. (Zittauer Maschinenfabrik.)

employed in series. For indigo dyeing "dipping vats" are also frequently employed in which the cloth is mounted on frames that are lowered into the dye liquor, after which it is exposed to the air for oxidation.

Fig. 210 shows an arrangement of two jiggers for use in the dyeing of sulphur blue. The first is intended for dyeing, the second for washing the cloth, and an air passage for oxidising the dye is provided between the two jigs (see p. 545). These jiggers are provided with squeezing rollers.

Padding Machines, *i.e.*, machines for passing piece-goods through a concentrated solution, differ in principle from jiggers in having much smaller dye vessels or troughs. They are provided with squeezing rollers.

Machines similar in construction to the washing machine shown in Fig. 219 may also be employed in the dyeing of cloth, and like principles may also be adopted in the design of machines for the dyeing of warps.



VAT FOR HANK-DYEING

FIG. 211.

Yarn Dyeing.—Yarn is usually dyed by hand in the hank. For this purpose a rectangular vat, Fig. 211, is employed. It is fitted with the necessary pipes for filling and emptying, and a steam coil, usually perforated, is provided for heating. A false

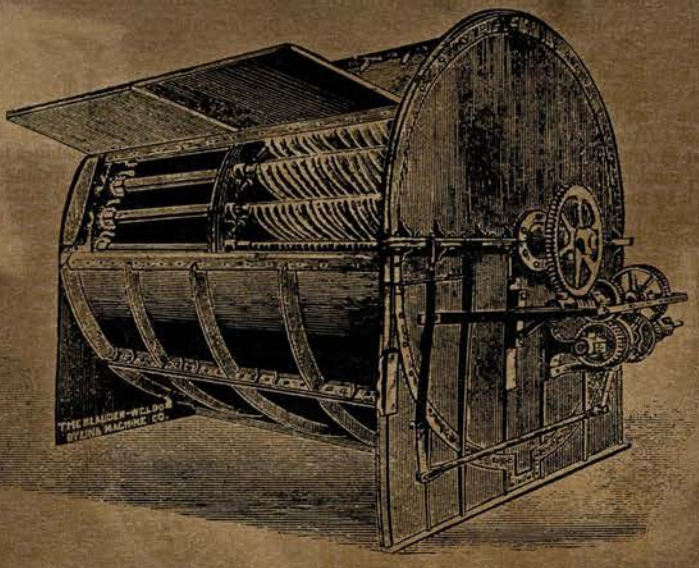


FIG. 212.—Hank Dyeing Machine for Sulphur Colours.
(Klauder-Weldon Dyeing Machine Co.)

bottom prevents the hanks from coming in contact with the latter. The hanks are suspended on square wooden rods placed across the vat, on each side of which stands a workman. One by one the rods full of yarn are taken up, and to each hank is given a quarter turn, so that the exposed part becomes submerged. This is carried out by means of a thinner rod which is inserted in the loop of the hanks immediately beneath the suspending rod. The rods are arranged in such a manner that there is always a sufficient space of about a foot available beside the rodful of hanks which is being turned.

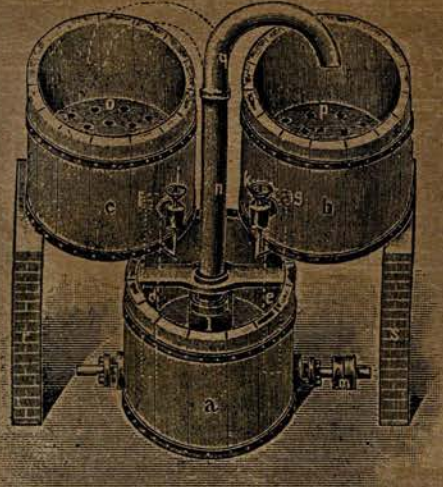


FIG. 213.—Dyeing Machine for Loose Wool, etc.
(Schirp.)

Numerous machines have been devised in which the motion given to the rods by hand is imitated mechanically. The plan most suitable for mechanical treatment seems to be the employment of a wheel on which the hanks are suspended by means of two series of rods, one series fitted near the centre, the other on the circumference of the wheel. The latter partially dips into the dye vat, and in turning slowly, alternately dips the hanks into the liquor and then lifts them out to drain; at the same time the sticks receive a rotary motion. The whole wheel is advantageously enclosed in a case fitted with doors. Fig. 212 shows a machine of this kind constructed by the Klauder-Weldon Dyeing Machine Co. This machine may also be employed for dyeing slubbing (combed wool) in the hank.

The Dyeing of Loose Fibre, Cops, etc.—Loose fibres may be dyed in suitable boilers in which they are turned by hand by means of poles. The material,

however, shows a considerable tendency to felt under these conditions, and mechanical appliances are, therefore, to be preferred.

The Klauder-Weldon Co. recommend a machine similar in appearance to the one described above for the dyeing of hanks. In it the material is placed in a perforated drum or wheel, which is divided into four sections or compartments and made to rotate inside a case in a similar manner to the wheel referred to above. In doing so, it alternately dips the fibres into the dye liquor and lifts them out to drain. The plan adopted by nearly all designers of dyeing machines for loose fibres, however, consists in placing the material in a perforated vessel or cage and forcing the dye liquor through it by means of a circulating pump, or by some other means. In many machines the direction of circulation can be reversed at will in order to ensure perfect uniformity of penetration. As a rule cotton is packed more tightly than wool, and a greater pressure of the circulating liquor is therefore necessary. Fig. 213 illustrates a simple machine for the dyeing of loose wool, etc. The material to be dyed is placed in one of the tubs *b* or *c*, of which one may be charged while dyeing is proceeding in the other. These tubs are fitted with a false bottom. The dye liquor is made up and kept continually heated in the tub *a* placed below *b* and *c*. The interior of the tub *a* is provided with a cataract pump which delivers large volumes of liquor through the pipe *n* and the movable

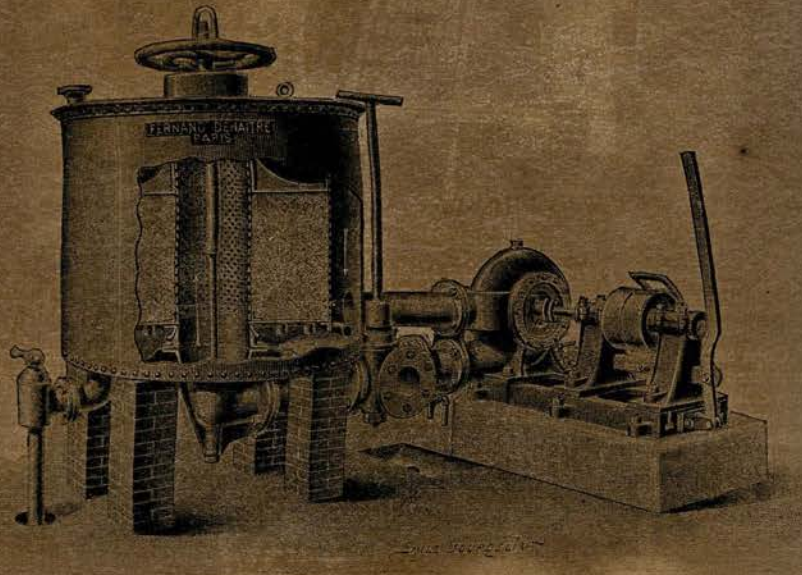


FIG. 214.—Dyeing Machine for Loose Fibres (Obermaier Type). (Dehaitre.)

connecting piece *q*. The latter may be turned so as to deliver on the top of the material contained in either of the dye vats *b* or *c*. This liquid then runs back again to the tub *a* through pipes fitted to the bottom of *b* and *c*, thus producing continual circulation. The goods are covered by a sieve and a spreader for the dye liquor, and the vats *a* and *b* are kept covered during use. This same apparatus may be provided with pipes to allow circulation of the liquid to proceed alternately from above and below.

A machine very frequently employed for the dyeing of loose cotton and wool is the Obermaier apparatus. In machines of this type (Fig. 214) the material is placed in a perforated drum, with a central perforated tube. This drum is fitted inside the dye tank proper, and can be removed at will for charging. Circulation of the liquor is produced by means of a centrifugal pump in the direction shown by the arrows.

Fig. 215 shows a machine charged with cops U and cross-wound bobbins V, which is also constructed in a slightly different manner for the dyeing of loose fibre. Like the Obermaier apparatus it consists, in the latter case, of a movable drum I for holding the material through which dye liquor is forced by means of the pump G. The drum is placed in the dye vat B which has a detachable front. In this apparatus the shell of the drum is not perforated, but it is divided into three compartments by perforated walls. The central compartment serves for distributing the liquor, the outer two for holding the fibre. The pump is double-acting, so that the direction of circulation can be reversed at will.

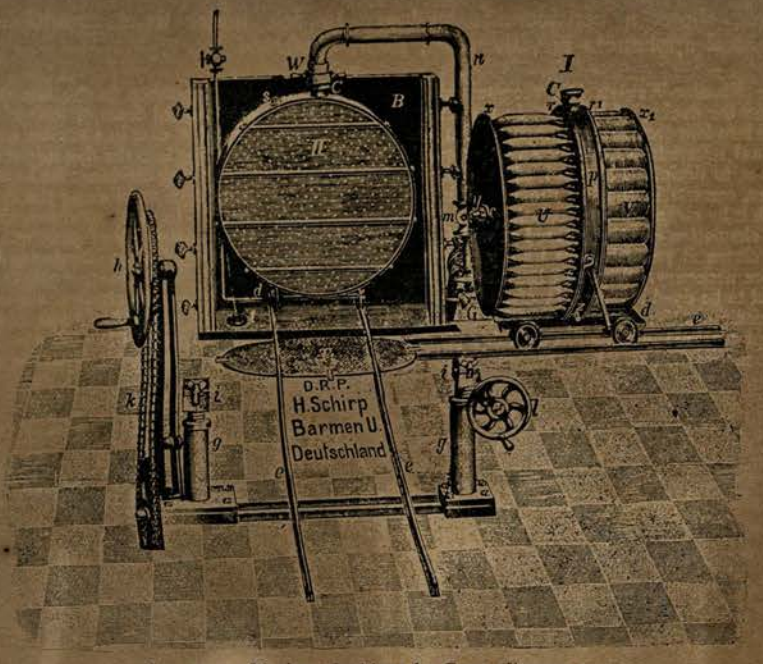


FIG. 215.—Dyeing Machines for Cops, Cheeses, etc.
(Schirp.)

Cops and cross-wound bobbins may be dyed by the "packing" system in machines similar to those used for loose cotton. In this case solid wooden skewers must be inserted to prevent them from collapsing, and all spaces must be very evenly packed by means of some packing material such as loose cotton, etc. A method that leads to satisfactory results much more easily is the hollow perforated skewer system. In this system each cop or cross-wound bobbin is placed on a perforated paper tube on a perforated spindle or skewer, and the dye liquor is forced or sucked through the

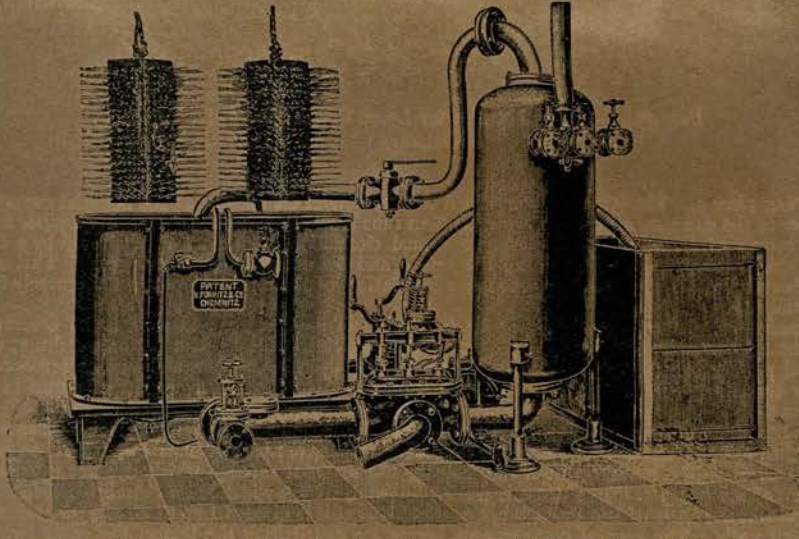


FIG. 216.—Dyeing Machine for Cops, Cross-wound Bobbins, Loose Fibres, etc.
(Pornitz.)

cop either directly by means of a pump, or else compressed air or vacuum or steam is employed for this purpose. Fig. 216 illustrates a machine of this type in which the cops or cross-wound bobbins are mounted on cylinders. In the machine already described, Fig. 215, they are inserted between two perforated metal plates, and Fig. 217 illustrates a cop-dyeing machine in which the cops are mounted on a square perforated plate.

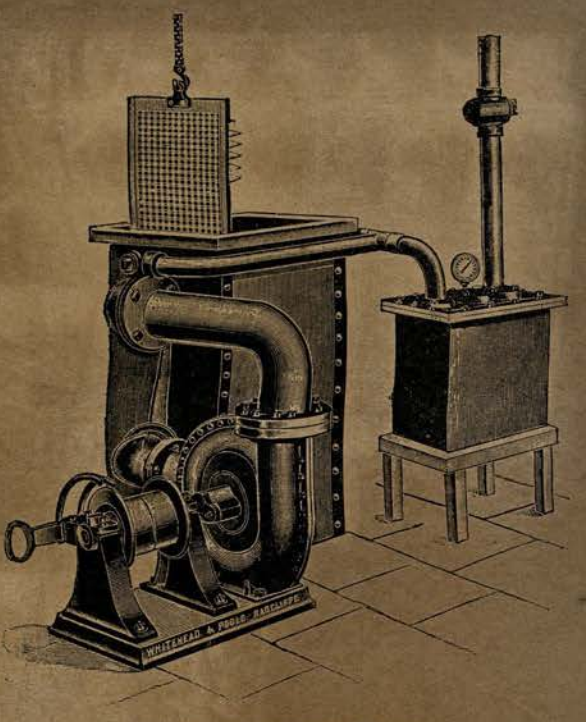


FIG. 217.—Cop-Dyeing Machine.
(Whitehead & Poole.)

Washing. — After dyeing, the goods must in nearly all cases be washed in water. Machines of similar or of identical construction to those used in dyeing may usually be employed. In all those cases already described in which the liquor is circulated by means of a pump, the dye liquor is usually simply withdrawn from the vat without removal of the goods and replaced by water. Most of the washing machines described in the chapter on bleaching may also be employed by the dyer. In the washing of cotton piece-goods it is often desired to cause the scouring liquor to impinge with considerable force against the cloth. For this purpose so-called beaters may be employed. These may be described as scoops which rotate rapidly on the surface of the liquor and throw it with considerable force against the cloth. Fig. 218 illustrates the action of such beaters, and Fig. 219 shows a washing machine fitted with beaters. In this figure a vertical drying machine is also shown on the right. It will be seen that the calico passes through various tanks over guide rollers alternately placed in and above the liquid. Squeezing rollers are provided.

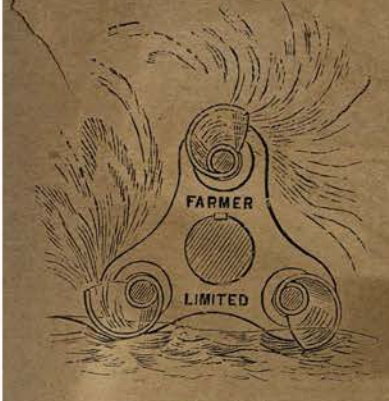


FIG. 218.—Beaters.
(Farmer.)

Drying.—The process of drying may be said to consist of two operations, firstly, the removal of as much water as possible by mechanical processes, and secondly, the evaporation of the remaining moisture. The former operation may be carried out by squeezing or wringing. A more thorough method for the mechanical removal of liquid, however, consists in throwing off the drops by centrifugal force. For this purpose so-called hydro-extractors are employed. These are machines which consist essentially of a perforated metal cage for holding the goods, which can be rotated very rapidly around a vertical axis by an electric motor or otherwise

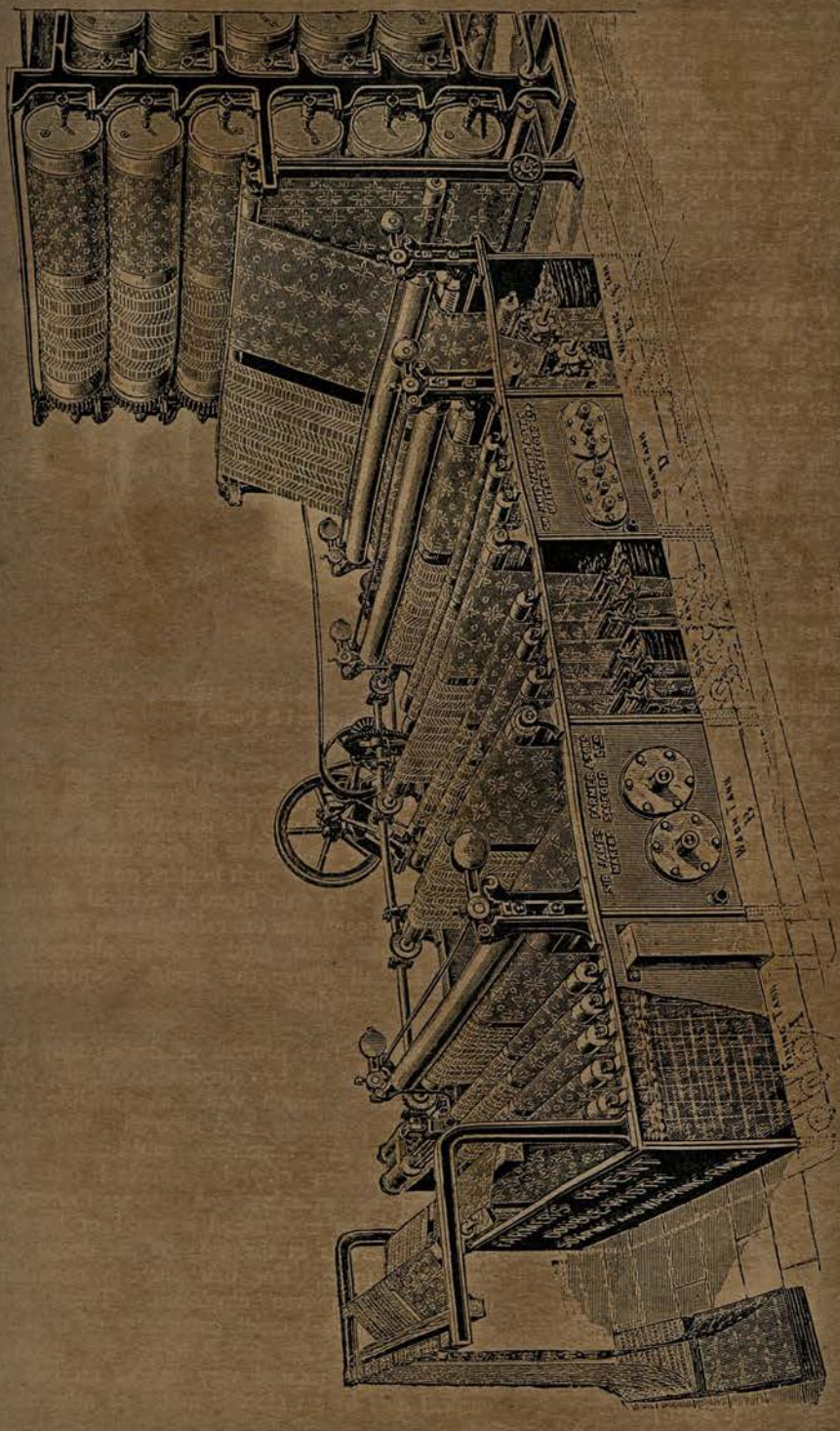


FIG. 219.—Washing Machine and Vertical Drying Machine. (Farmer.)

(see Figs. 220, 64, 65). The liquid is collected in a casing which usually forms part of the framework of the machine.

For the final drying of the fibres by evaporation, artificial heat is usually applied, although drying at ordinary temperature is sometimes carried out.

oose fibres are usually dried in a ne consisting essentially of a cham- rough which the fibres travel on an s band, meeting a countercurrent air during their passage.

is usually dried by suspending s on poles or movable frames in constructed drying ovens through ow current of hot air is passed. cross-wound bobbins may be similar manner, or else the ing system may be employed in conjunction with the wn in Fig. 217. The cops he cylinders which are put chines in which hot air can ough the cops.

is usually dried by passing it rds over steam-heated rollers 219). The final drying is fre- rried out in stentering machines . In these the cloth which has shrunk slightly in the processes of dyeing is brought back to its original width by stretching slightly. For this purpose the moist cloth is passed between two moving endless chains which grip it at the selvedges by means of clips. These chains are not parallel but diverge slightly so that the cloth is stretched during its passage between them. At the same time it is dried by hot air drawn over steam pipes.

FIG. 220.—Hydro-Extractor.
(Dehaitre.)

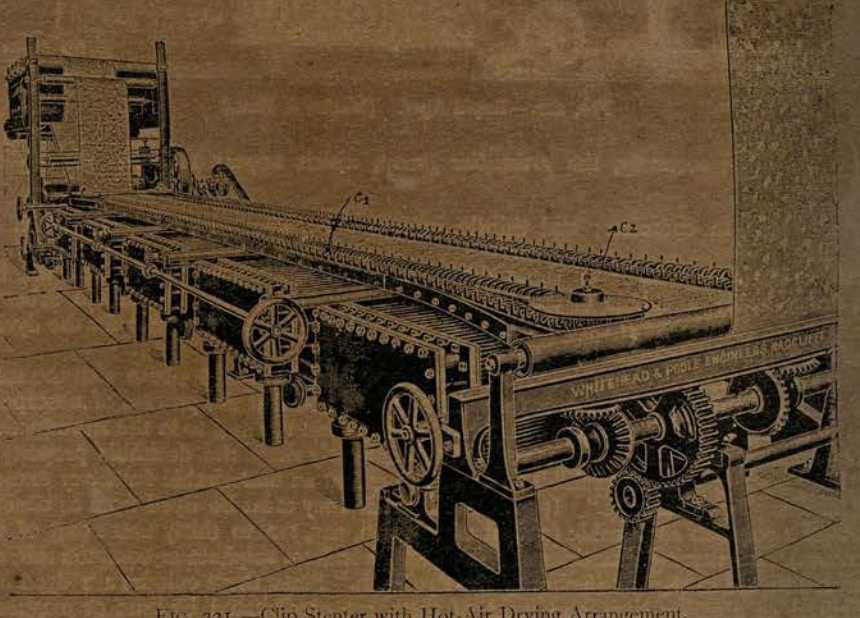


FIG. 221.—Clip Stenter with Hot-Air Drying Arrangement.
(Whitehead & Poole.)

Before leaving the subject of dyeing machinery, a brief reference must be made to the **agers** employed particularly in the development of **aniline black**, pp. 480, 556 (and also for the fixation of printed colours). These consist of chambers containing a hot atmosphere heavily charged with steam in which the cotton cloth can be hung or through which it can be passed continuously over rollers. Fig. 222 illustrates a **rapid ager** for aniline black. It is fitted with heating coils and perforated pipe for the supply of steam. The roof and the guide rollers near the common inlet and exit of the cloth are heated by steam to prevent the formation of drops of water which would soil the goods.

Direct Dyes

The simplest dyes, from the dyer's point of view, are those which are taken directly from their solutions by the fibre.

Direct Cotton Dyes.—During the last three decades a large number of direct cotton dyes have been put on the market. The dyes of this class seem to belong to a few well-defined groups of chemical compounds. We have the congo-red group, the members of which contain the tetrazo grouping

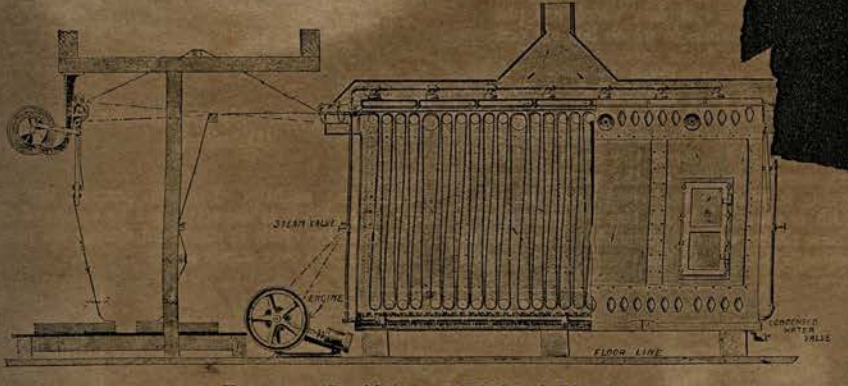
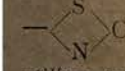


FIG. 222.—Rapid Ager. (Mather & Platt.)

$\left\{\begin{matrix}-N=N- \\ -N=N-\end{matrix}\right.$; secondly, the *primuline group*, which appear to have the radicle



—in common; and thirdly, various dyes, which may be classed as *di-stilbene-azo-dyes*. Most of these dyes are also taken up by wool and silk, but a few, notably members of the last-named group, hardly dye the animal fibres at all. The direct cotton dyes are thus of particularly great importance for the dyeing of union goods, satins, etc.

The fact that these substances are not taken out of the dye-bath with the same degree of avidity as direct dyes for wool and silk, and that the process of absorption is of a more or less reversible nature, has already been referred to in the Introduction. On account of these circumstances they eminently show the desirable property of "level dyeing," but also exhibit to a marked extent an undesirable tendency towards "bleeding" or "running." It follows also that they must be dyed from as concentrated a solution as possible (weight of solution, say, ten to thirty times that of the cotton), and varying quantities of salts, such as sodium sulphate or common salt, are added to aid in the exhaustion of the dye bath. Since these colours are dyed in a neutral or alkaline bath, and most of them are precipitated by lime or magnesia, it is necessary to soften hard water before use. This is most conveniently done by

boiling with a small amount of soda ash. As a rule the goods are entered at medium temperature, and dyeing is carried on at the boil, but dyeing at low temperatures is also sometimes carried out. The dye baths are not exhausted, and may be used over again after making up to strength by the addition of the necessary amount of dyestuff.

The following are two of the processes which may be employed :—

1. **Process at Boiling Temperature.**—Work the cotton at the boil for one to one and a half hours, adding 5-30 per cent. (on weight of cotton) of crystallised Glauber's salt, or 2½-10 lbs. of common salt.

The salt aids in the exhaustion of the bath but rather hinders boiling, and if difficulties are met with in this respect its quantity must be reduced, or it must be replaced by soap, turkey red oil, etc. After removal from the bath the goods are wrung and then rinsed in cold water, soda solution, or turkey red oil.

2. **Cold Bath.**—Stir the dyestuff with an equal weight of caustic soda solution of sp. gr. 1.35-1.38 (70-76° Tw.), and dissolve the whole in boiling water. Enter the cotton into the bath when cold or lukewarm and dye with the addition of a little soap and, if necessary, Glauber's salt.

The following are some of the names and prefixes employed by various firms to indicate their direct cotton colours: Benzo-, Congo-, Diamine, Union, Direct, Purpurine, Diamol, Chlorazol, Ingrain, Sultan, Titan, Primuline, Sulphine, Oxamine, Pyramine, Thiazine, Phenamine, Chrysamine, Oxyphenine, Chrysophenine, Curcuphenine, Zambesi, Chicago, Columbia, Hessian, Triazol, Toluylene, etc.

After-treatment of Direct Cotton Dyes.—The direct cotton dyes are eminently suitable for after-treatment on the fibre, whereby not only new shades are produced but very much faster colours are obtained.

Basic dyes may be dyed upon them as on mordants (p. 549), or they may be converted into new "**ingrain**" **colours** by the process of diazotising or coupling (pp. 442, 450, 478, 558).

Many of them are also greatly improved by after-treatment with metallic salts, such as copper sulphate, chromium salts, and the bichromates of sodium and potassium (p. 553).

Another method of after-treatment which has a marked effect on the fastness to washing and milling of certain dyes consists in working the dyed cotton for about half an hour at 60° in a bath charged with 1-3 per cent. formaldehyde (40 per cent.).

Wool and Silk are both frequently dyed with the direct cotton colours, the former in neutral or very feebly acid baths containing Glauber's salt at boiling temperature, the latter in a neutral boiled off liquor bath, the fibre being entered at lukewarm temperature and the bath being gradually taken to boiling temperature. After dyeing has proceeded for about an hour, the bath is usually made feebly acid with acetic acid to aid exhaustion.

The dyes may be subjected to after-treatment as on cotton, and the silk is finally brightened by passing through a very dilute solution of acetic or tartaric acid * and dried without washing.

Sulphur Colours

The sulphide or sulphur colours which have become of great importance in recent times for obtaining fast shades on cotton or other vegetable fibres, form a group of dyes that are obtained by fusing sodium sulphide, or a mixture of sodium sulphide and sulphur with various organic substances. They are insoluble in water and are dyed from a solution in sodium sulphide. Many of them are reduced by the bath and presented to the fibre as more or less coloured leuco compounds, being afterwards oxidised by contact with the air. They will readily dissolve in alkaline reducing agents, and may occasionally be dyed in the vat like indigo.

* The brightening of silk by treatment with acid is due to the fact that silk absorbs acid and retains it tenaciously, whereby its lustre is increased and it acquires the property of emitting a crackling sound called the scroop of silk when it is twisted and pressed together. The rustling of silk garments is doubtless due to this property. Tartaric acid being retained more permanently than the other acids, is the most efficient, but the most expensive of the acids employed.

They may be employed for dyeing artificial silk and also silk and wool, but the animal fibres, more especially wool, are liable to attack by the alkaline sulphide solutions unless protected by special previous treatment. The dyes are occasionally employed in the dyeing of unions. These colours are distinguished by good fastness to light, washing, cross-dyeing, etc., and they do not bleed like the direct cotton colours.

It has occasionally been observed that the cotton fibre has become tendered on storing after dyeing with the sulphur colours, and this has always been associated with the formation of sulphuric acid. When this difficulty occurs, it is best met by subjecting the cotton to an after-treatment with a feebly alkaline substance, such as soap, sodium acetate, or carbonate. A very suitable process appears to be that recently patented by Holden, in which calcium tannate is deposited on the fibre after dyeing, by steeping the material for a few minutes in tannic acid at about 40° C., squeezing, passing through limewater, and washing. The calcium tannate being insoluble has the advantage of not being liable to be removed on washing like the feebly alkaline substances mentioned above. After dyeing, the material should in all cases be wrung well and rinsed thoroughly.

In dyeing with these colours, vats made of wood or iron may be employed. Copper or any alloys containing this metal must be carefully excluded, as this metal goes into solution rapidly in the sodium sulphide solutions, and the copper compounds formed, lead to oxidation of the dyestuff and irregular dyeing. The fibre should be kept submerged, and yarn may conveniently be dyed on bent iron pipes, the ends of which have been wrapped round with cloth.

The dyestuff, to which has been added about three or four times its weight of crystallised sodium sulphide and some soda ash, is dissolved in a small amount of boiling water with stirring, and the solution obtained, is added to the bath, which usually contains an amount of water equal to about twenty to thirty times the weight of the cotton. The amount of soda ash employed is about 5 per cent. of that of the cotton, and the bath contains 10-60 per cent. (on the weight of the cotton) of common salt according as a light or dark shade is required. For dark shades the cotton may be entered at boiling temperature, turned several times, and allowed to steep for several hours. For lighter shades a lukewarm or even a cold solution may be employed and a shorter time is requisite. Turkey red oil is sometimes added to the bath to secure more even dyeing. Certain sulphur dyes, such as the kryogene blues, must be developed by oxidation in air at a high temperature in the presence of moisture, by steaming in the presence of air, or by storing in a damp warm place.

An after-treatment with oxidising metallic salts, viz., with a solution containing, say, 2 per cent. of potassium bichromate, 2 per cent. of copper sulphate, and 3 per cent. of acetic acid on the weight of the cotton at about 70° C. improves the fastness of some of these dyes.

Like the direct cotton colours they act as mordants for basic colours, and many of them may be coupled with diazo solutions (p. 558). The first dye of this description known, viz., Cachou de Laval, was discovered a considerable number of years ago. The following are some of the names employed by various firms to indicate the newer sulphide dyes: Amidazol, Crossdye, Immedial, Katigene, Kryogene, Pyrogene, Sulphur Thiogene, Thion, Thionol, Thioxine.

Natural Direct Dyes for Cotton.—Several natural dyes, such as turmeric, safflower, and annatto, are direct dyes for cotton.

ACID DYESTUFFS

This class comprises all those dyestuffs which are of an acid nature. It is obvious that some of these colours may belong to the class of direct cotton dyes, others may often be employed in conjunction with mordants, and thus the various classes of dyes merge into each other. The acid dyes are either nitro compounds or sulphonic acids, and in nearly all cases they are sold in the form of sodium or occasionally calcium salts. In many cases they have been obtained from basic dyes by introducing the sulphonic group of atoms.

Cotton.—Generally speaking the acid dyes will only stain cotton and other vegetable fibres very slightly, so that only very light and fugitive shades can be obtained by direct dyeing even when concentrated baths are employed. The results

are somewhat better when the dyes are used in conjunction with gelatine or basic mordants, such as alumina or stannic oxide, but even so, the shades obtained are not fast to washing.

Wool.—The acid dyes are of the very greatest importance in the dyeing of wool. The wool is always dyed at boiling temperature, and a quantity of sulphuric acid is usually added, which is very much in excess of what is required to liberate the free colour acid from its salt. That the object of this acid is to produce lanuginic acid from the wool, which latter substance is primarily dyed, has already been mentioned in the Introduction. The mineral acid might thus be termed a "mordant" (*i.e.*, biting agent), using the word in the significance in which it was originally, though wrongly, employed by the dyers of former times.

Sodium sulphate or bisulphate is nearly always added as a levelling agent, since this substance appears to have a slight solvent action on the dye taken up by the fibre, thus removing it from those places in which it may have been deposited in excess, and generally retarding the operation of dyeing. When dyestuffs are employed which dye with exceedingly great rapidity, the sulphuric acid is replaced by acetic acid or by ammonium sulphate or acetate, substances which slowly become acid in the boiling bath owing to the expulsion of ammonia. In certain cases, particularly in the dyeing of unions, a boiling neutral bath is employed. Stannic chloride or alum is sometimes added in small quantity; tin oxide or alumina will thus be deposited on the fibre from the boiling bath, and by taking up colour from the solution increase the brilliancy of the shade. Certain acid dyestuffs, viz., the alkali blues, are not soluble in dilute acids and must be dyed from a feebly alkaline solution. The wool is afterwards treated in a hot bath containing dilute sulphuric acid. The colourless sodium salt which is originally taken up is thus converted into the blue acid.

The following may be taken as an example for the dyeing of 100 kg. of wool.

Employ a bath (5,000-10,000 l.) containing 1-4 kg. of concentrated sulphuric acid, 10-20 kg. of Glauber's salt crystals and the requisite amount of dyestuff, enter at about 70° and heat to the boil, leaving the wool in the boiling bath for about an hour.

Silk.—The acid dyes are of considerable importance in silk dyeing, although they are not fixed so well as on wool.

A bath is usually employed containing 20-30 per cent. (on volume of bath) of boiled-off liquor, which is slightly acidulated with sulphuric or acetic acid. The silk is usually entered at lukewarm temperature and dyed slightly below boiling. It is then washed with water and brightened by means of sulphuric, acetic, or tartaric acid, and dried without further washing.*

The following are a few of the more important names met with among the acid dyes: Naphthol yellow, Tartrazin, Fast yellow, Tropæolin, Brilliant orange, Brilliant scarlet, Xylidine scarlet, Biebrich scarlet, Crocein scarlet, Fast red, Archil substitute, Orseillin, Acid magenta, Acid eosin, Acid rhodamine, Acid phloxin, Acid violet, Alkali violet, Sulphone azurin, Alkali blue, Soluble blues, Patent blue, Cyanine, Soluble induline and nigrosine, Naphthazine blue, Wool green, Naphthol green, Fast brown, Orcellin, Naphthol black, Naphthylamine black, Sulphone black, Wool black, Biebrich patent black.

BASIC DYES.

This important class, which comprises some of the most brilliant and beautiful colours known, consists of coloured salts of colourless acids and organic colour bases. When the animal fibres are dyed by these subtances, only the base is taken up in a coloured form, as explained in the introduction, the acid being left behind in the bath.

Cotton.—Cotton is nearly always dyed with the intervention of an a mordant, and the processes employed will, therefore, be considered later in c junction with those used for mordant dyes (pp. 548, 550).

* See note, p. 545, also see p. 518.

Wool.—Although not so important as the acid dyes on account of their fugitiveness, yet the basic dyes still possess a considerable amount of importance in the dyeing of wool. They are in most cases dyed from a very feebly acid bath, but a soap bath is also sometimes employed when very soft water is available. That hard water must be feebly acidified, preferably by acetic acid, has already been mentioned under the heading of **Water**. No other addition is made.

The bath is usually started cold and gradually raised to the boil. Dyeing is continued until the bath is exhausted, which sometimes takes place before boiling. The goods are well washed after dyeing. Owing to the great tinctorial power of these dyes a very small amount is usually sufficient, ½ per cent. on the weight of the wool usually producing a medium shade. The colours should be filtered through cloth before adding to the dye bath as a precaution against the introduction of undissolved particles.

Silk.—On account of their brilliance the basic dyes play an important part in silk dyeing in spite of their fugitiveness as a class. A neutral or slightly acid bath may be employed consisting of one-third boiled-off liquor and two-thirds water. The same general precautions must be taken as in the dyeing of wool.

The silk is usually entered cold and the temperature gradually raised to a little under boiling. After dyeing, the fibre is rinsed and brightened by means of tartaric or acetic acid.*

A bath containing about 1½-2 per cent. (on the weight of the silk) of soap is frequently employed for dyeing pale shades at a temperature of 30°-40° C. (85°-105° F.).

The following are a few of the best-known basic colours: Magenta, Safranine, Magdala red, Chrysoïdine, Phosphine, Auramine, Methyl green, Malachite green, Diphenylamine blue, Victoria blue, Methylene (ethylene) blue, Meldola's blue, Nile blue, Indulines and Nigrosines, Methyl violet, Crystal violet, Mauve, Bismarck brown, Fast black.

The rhodamines, including irisamine, etc., also belong to this group, and the weakly acid eosins, including erythrosin, phloxin, rose bengal, may be dyed by similar methods.

MORDANT DYES

The mordant dyes are basic or acid substances which are not fixed on the fibre directly, but are caused to combine with a compound of an acid or basic nature termed a mordant which has usually been previously deposited on the fibre. The compound formed is termed a colour-lake.

Some dyes, such as alizarin or logwood, are only feebly coloured before combination, and yield different shades with different mordants. These are termed **polygenetic dyes**. Others have the property of dyestuffs before combination, and their lakes do not usually differ much from them in colour. These are "**monogenetic**" **dyes**.

Acid Mordants.—These mordants are of the greatest importance for the fixation of basic dyes, particularly on cotton. They are also frequently employed in order to fix basic mordants on other fibres, and in silk weighting. The most important are the tannins and the oil mordants.

The **tannins**† form a class of compounds which are distinguished by the fact that they are taken up readily by the animal skin, causing it to be tanned. Most of them are colloids, and their more important properties are doubtless closely connected with this circumstance. They will combine with basic dyes producing compounds insoluble in water but soluble in an excess of tannic acid. When brought together with salts of heavy metals containing a feeble acid a precipitate is formed ontaining the metal oxide and the tannin. This precipitate which is insoluble in tannic acid is obably what is termed a colloid compound, *i.e.*, a compound produced by the phenomenon of dsorption" between a colloid bearing a positive and a colloid bearing a negative electric charge en in solution. These precipitates have the property of combining with basic dyes, forming the oured so-called "triple" compounds which constitute the lakes employed in dyeing cotton with ic dyes.

* See p. 545. † See also pp. 490 and 573.

The most important tannin is tannic acid or gallo-tannic acid, a substance obtained commercially on the large scale by the extraction of nut galls. This substance should be exclusively employed for dyeing pale shades on cotton; for dark shades the more or less coloured extracts of the following substances containing tannin may be employed—sumach, myrobalans, divi-divi, valonia, chestnut, etc. The bath is prepared according to the amount of colour to be fixed with quantities of tannic acid, varying, say, from ½-8 per cent. on the weight of the cotton, allowing sufficient water to work the material conveniently. For pale shades the material, which must have been carefully freed from air by boiling out, is worked for a half to one hour in the bath; for darker shades the material may be entered at boiling temperature and then allowed to steep in the cooling bath for twelve hours. It is then worked in a tartar-emetic bath containing, according to the amount of tannin to be fixed, ·4 per cent. (on the weight of the cotton) of tartar-emetic for about a quarter of an hour. The insoluble antimony tannin compound referred to above is thus produced. The excess of antimony salt must be very carefully washed out or preferably removed by passing the dyed goods through another tannin bath. Aluminium, iron, or stannic salts are also employed for the fixation of tannic acid.

Turkey-red oil, Alizarin oil, Sulphated oil, Soluble oil,* are names applied to another class of acid mordants which are sometimes employed for fixing basic dyes on cotton. Their principal importance, however, lies in their application to the fixation of basic mordants in turkey-red dyeing. As will have been seen from the prescriptions given for dyeing with various direct dyes, turkey-red oil is also frequently employed as an assistant in the place of sodium sulphate where difficulties are met with in obtaining level shades.

Turkey-red oil is formed by the action of concentrated sulphuric acid at medium temperatures on various oils, such as olive oil, cotton-seed oil, and castor oil. The last-named is by far the most important. The products formed are distinguished by the fact that they are soluble in water, while they retain to a certain extent the properties of the oils from which they have been produced. Chemically, turkey-red oil is probably a mixture of various primary ethereal salts of sulphuric acid. It has the great advantage over ordinary soap that its salts with the alkaline earths are not sticky substances but fine powders which have no tendency to cause uneven dyeing.

In mordanting cotton, the material may be saturated with a solution containing 50 g. of turkey-red oil per litre, wrung, dried, and then treated for half an hour in a tepid solution of aluminium acetate of sp. gr. 1.015 in order to fix the mordant.

Dyes as Mordants.—The fact that basic dyes may be dyed on cotton on other dyes, which may thus in a certain sense be considered to be acid mordants, has already been referred to (pp. 545, 546).

Dyeing Basic Dyes on Cotton.—The basic dyes are usually dyed on mordanted cotton in the cold or at temperatures up to about 70°. A feebly acid substance, such as acetic acid or alum, is usually added to retard dyeing in order that even results may be obtained, and the dye solution is usually added during dyeing in intervals of about a quarter of an hour in about three or four portions. The operation is usually started in the cold and completed at about 60° C.

Catechu.†—In conjunction with the tannins reference must here be made to the exceedingly important natural dyes, catechu or cutch and gambier. These substances contain varying amounts of a tannin called catechutannic acid and a white crystalline substance known as catechin. In addition they contain a brown dyestuff formed by oxidation of the preceding.

Cutch and gambier are employed largely in cotton and to a certain extent also in wool dyeing. The material is usually immersed in a boiling bath of the dye containing about 10 per cent. of copper sulphate (of the cutch employed). The latter acts as an oxidising agent and probably also as a mordant. The material is then allowed to steep for several hours and afterwards treated with a hot bath containing about 2 per cent. of dichromate. This substance effects a further oxidation.

Catechu and gambier are also used in large quantity in silk weighting.

* See p. 43. † See p. 486.

Dyeing in Conjunction with Basic Mordants

Nearly all insoluble metal hydroxides may be deposited on the textile fibres as mordants, for the purpose of obtaining colour-lakes with various dyes. A brief survey of the more important methods employed for the various classes of fibres, and a short reference to the dyes used, some of which are among the most important known, is all that can be attempted here.

Wool.—Wool is capable of dissociating the salts of heavy metals at boiling temperature, taking up both the metal hydroxide or a basic salt and the acid, the former in an insoluble form, the latter in a form in which it can be washed out by water. This fact is made use of in the mordanting of wool. It is necessary to employ such salts as are not dissociated hydrolytically by the boiling water to an appreciable extent or else to hinder this dissociation by the addition of suitable substances. The deposit of metal hydroxide formed would otherwise not be held fast by the fibre. Thus in mordanting with aluminium sulphate it is necessary to make an addition of sodium bisulphate, sulphuric acid, or preferably of cream of tartar or of some other substance of an acid nature.

The following prescription for alumina may be taken as an instance of the mordanting with salts such as aluminium sulphate, chromium fluoride, ferrous sulphate, etc. Employ a bath containing about 8-10 per cent. of alum and 2½-5 per cent. of tartar (on the weight of the wool), enter at a low temperature, heat gradually to boiling and maintain at the boil for about half an hour. After cooling, the wool is thoroughly washed or preferably boiled in water to remove as much of the acid as possible. It is then dyed without allowing it to dry.

A very important mordant for wool that calls for a few special remarks is potassium (or sodium) **bichromate** (bichrome or chrome). The substance to be deposited on the fibre in this instance is chromic oxide, and reduction of the chromate originally taken up is therefore necessary. When chromate alone is employed, this reduction is probably effected to a small extent by the wool itself. The latter, however, still shows the yellow colour of chromate on leaving the mordanting bath, and the principal reduction no doubt takes place in the dye-bath later on.

It will be readily understood that care is necessary in the use of this mordant owing to its oxidising properties in order that "overchroming" of the wool may be avoided. According to Knecht, the chromate is taken up by the wool as chromic acid, and the bath consequently shows a tendency to become alkaline. If used over again it should therefore be made up to strength by the addition not only of bichromate, but also of the necessary amount of sulphuric acid.

For high-class goods bichromate is frequently employed in conjunction with reducing agents, of which cream of tartar, oxalic acid, formic acid, and lactic acid are the more important.

The following may serve as a prescription for the mordanting of wool with bichromate. Boil the wool in a bath containing 2-4 per cent. bichromate (of weight of wool). Water, fifty to a hundred times the weight of the wool. Time, one to one and a half hours; then wash with water and dye without drying.

Basic Mordants for Silk.—Silk is usually mordanted at medium temperatures at which the metal salts employed are not decomposed by the fibre. It thus becomes necessary to pass the latter through the solution of a fixing agent, such as sodium silicate, which deposits an insoluble basic precipitate on the silk. Instead of this, the fibre may in many cases simply be washed very thoroughly with water, which produces an insoluble precipitate by the process of hydrolysis. In the mordanting of silk with iron and tin salts tannin is usually employed as a fixing agent. A soap bath also has a similar effect. By passing the fibre alternately through baths containing the metal salt and the tannin extract, the fibre may be "weighted" up to about four times its weight with the metal tannate. This fact is made use of in dyeing silk with heavy logwood blacks.

Basic Mordants for Cotton.—Although cotton may absorb a certain amount of metal salts, it can in no way decompose them. Either a salt such as the acetate must be employed which can be decomposed or hydrolysed by heating, yielding a basic salt; or else a fixing agent, *i.e.*, a substance which yields a precipitate of basic properties when added to a solution of the salt in question, must be employed.

In the former case the impregnated goods are subjected to the process of "ageing," which consists in exposing them to a warm moist atmosphere.

In the latter case the cotton may either be treated with tannin or some other acid mordant taken up directly by the fibre and then be passed through an alkaline bath and through the metal salt solution, or else the material is first passed through the metal salt solution and then treated with a fixing agent, such as ammonia, caustic soda, chalk, sodium carbonate, silicate, phosphate, or arsenate, which yields a precipitate of strongly basic properties by interaction with the salt in question.

When employing turkey-red oil or tannic acid, the cotton is first impregnated as described under acid mordants, it is then usually passed through clear lime water to neutralise the acid and afterwards worked in the salt solution for about an hour. It is usually finally passed through a weak soap bath, thoroughly rinsed in water, and then dyed.

When one of the alkaline fixing agents indicated above is employed, the cotton is usually treated for several hours with the mordant solution, wrung out, dried at a low temperature, then worked for about half an hour in the solution of the fixing agent at medium temperature, thoroughly washed, and then dyed.

The Dyes

Although mordant dyes, both natural and artificial, are among the most important known, yet all that can be attempted here, is a brief enumeration of them, and an indication of the mordants with which they are applied.

Logwood.—This substance consists of the heart-wood of a tree known botanically as *Hæmatoxylon campechianum* which grows in various parts of America. The wood is subjected to a process of fermentation and oxidation called "ageing" or "maturing," during which a glucoside originally present in it is decomposed into a sugar and a substance called hæmatoxylin. The latter on oxidation yields a body named hæmatein which is the colouring principle of logwood. The dye is bought by the dyer either as chips, as decoctions, known as logwood liquor, or as extract, i.e., a paste obtained by evaporating the decoction. In the former case it is extracted by the dyer himself by means of boiling water. Logwood is employed for dyeing both vegetable and animal fibres, and its importance lies chiefly in the production of fast blues and blacks on the latter (see also pp. 484, 490).

When employed for dyeing blacks on **cotton** it is usually applied in conjunction with an iron mordant fixed by tannin.

The following prescription may serve as an example. Work the cotton in a cold infusion of about 30-40 per cent. of sumach (of weight of fibre), allow to steep for several hours, and without rinsing work for about half an hour in a cold solution of "nitrate" of iron (*i.e.*, ferric sulphate), of sp. gr. 1.01-1.02, treat with a cold chalk bath to remove excess of acid, and wash thoroughly. Dye in a bath containing logwood and a little fustic (say 8 per cent. solid logwood extract and 1½ per cent. of fustic extract of sp. gr. 1.25), then treat with a bath of about 1½ per cent. copperas, or with a warm bath containing potassium bichromate (say ½ g. per litre) in order to remove the excess of logwood. Then work in a solution of soap, say 5 g. per litre, at a moderate temperature, squeeze and dry.

Chrome blacks may also be obtained on cotton; a purple is obtained by means of tin, a blue by means of a copper mordant.

Wool is dyed black by means of either an iron or chrome mordant.

The following prescription may serve as an example. Mordant in a bath containing 3 per cent. potassium bichromate, 8 per cent. tartar, and 5 per cent. sulphuric acid (of weight of wool) at boiling

temperature for about an hour, wash well and dye in a boiling bath prepared from 50-80 per cent. logwood and 5-10 per cent. fustic for about an hour, having entered the wool at about 80° C. An addition of about 5 per cent. alizarin improves the fastness of the shade to light. Then fix the excess of logwood taken up in a finishing bath containing about 1 per cent. of potassium bichromate at about 80° C. Wash and dry.

In order to produce logwood blues on wool, smaller quantities of dye and mordant are employed, and the fustic is omitted in the dye bath.

Silk.—Logwood blacks play an important part in the dyeing of silk. As a rule the logwood is dyed on an iron tannin mordant, and other substances are incorporated with the dye, allowing it to weight the silk up to about 400 per cent.

The following prescription, by means of which iron tannate, tin tannate, Prussian blue, catechu, and logwood are all fixed on the fibre, allows a weighting up to about 100 per cent. and may serve to illustrate the process.

Mordant with basic ferric sulphate, then soap. Repeat these operations one to eight times, according to the amount of weighting desired; dye Prussian blue by means of potassium ferrocyanide, treat with a catechu bath (100-150 per cent.) containing 10-15 per cent. stannous chloride at 60°-80° C. Treat with a second catechu bath containing no tin (100-200 per cent. catechu), mordant with pyrolignite of iron. Dye with logwood and soap. Brighten.

The following **natural mordant dyes** can only be referred to: Fustic (young fustic) and Quercitron bark (yellow on chromium mordant); Weld (yellow on chromium, aluminium, tin;—olive or olive-yellow on iron and copper mordant); Persian berries (yellow or yellowish olive on tin, copper, aluminium, iron;—brown on chromium mordant); Saunders wood, barwood, camwood (red to brown according to mordant); Cochineal, Kermes, and Lac dye (scarlet and crimson on tin and aluminium mordant) (see also **Natural Dyes**, p. 483).

Alizarin.—This exceedingly important dyestuff, which constitutes the principal colouring matter of madder, is at the present time obtained practically exclusively by artificial means from coal-tar (p. 451). The two substances, isopurpurin and flavopurpurin, are present in varying amounts in different brands of the commercial article and affect the shades of the dyed material to a certain extent. Alizarin is put on the market as a paste containing 20 or 40 per cent. of the dyestuff or as a powder containing from 80 per cent. upwards. Its most important application is to the production of turkey red on cotton.

It would be beyond the scope of this article to give a full account of turkey-red dyeing, but it may be stated briefly that the production of this exceedingly brilliant and fast colour is based on the formation of an exceedingly complicated aluminium-calcium lake of alizarin which contains also a certain amount of tannin and fatty oil. The latter is a decomposition product obtained by using either olive or turkey-red oil. In addition the lake often contains stannic oxide in small quantity. The following enumeration of the operations carried out in one of the simpler processes of turkey-red dyeing will give a general idea of the complicated nature of the method.

The cotton (300 kg.) is first freed very completely from fatty and resinous matter by "bowking" or boiling under a pressure of 2 atmospheres with caustic soda solution of sp. gr. 1.005 for four or five hours (p. 521). It is then treated successively three times with turkey-red oil and dried at 70°-75° after each treatment. The baths employed for this purpose are "standing" baths, and are freshened up as follows: The first oiling bath is freshened up with 22 kg. acid oil, 5 kg. ammonia, 22 l. of potassium carbonate solution of sp. gr. 1.26, temperature 40°-45° C. (For a fresh lot two and a half times these quantities are needed.) Second oiling bath like the first; the third oiling bath is freshened up with 20 kg. acid oil and 44 l. potash solutions. After drying, the cotton is now steeped for eight hours in water of 30°-35° C., hydro-extracted and again stoved at 70°-75°. It is now ready for the alum mordanting bath, which is freshened up with 50 kg. aluminium sulphate, 1.25 soda crystals, the same amount of chalk, and 1 kg. of tannic acid. The cotton remains in the bath for fifteen to twenty hours, is well rinsed and then passed wet into the dye bath. The latter contains about 20 kg. alizarin, 300 g. tannic acid, and about 1 kg. chalk. The material is treated in the cold bath for an hour; the latter is then slowly heated to boiling, and afterwards kept for about an hour. The material is then subjected to two successive processes of clearing by soap, first for three hours at 1½ atmospheres pressure with a solution containing 3-4 kg. of soda, rinsing and finally boiling at 1½ atmospheres with 8 kg. soap, ½ kg. soda, and 400 g. of tin salt (stannous chloride). It is then rinsed and dried in the air.

Alizarin is also dyed on cotton with chromium mordants for claret red and maroon shades, and on iron mordants for very fast violets.

Wool is dyed with alizarin on aluminium, chromium, iron, and tin mordants; red, maroon, violet, and orange shades respectively are thus produced. The mordants are applied as previously described.

In conjunction with the aluminium mordant 10 lbs. of 20 per cent. alizarin paste, 2 lbs. of calcium acetate, 1 lb. of soap, and ½ lb. of tannic acid may be employed per 100 lbs. of wool. The latter is introduced into the cold bath, which is then heated to boiling and kept so for an hour and a half. The mordant and the dye are sometimes dyed simultaneously from the same bath where only light shades are required (single bath method).

Silk may also be dyed with alizarin on aluminium, chromium, and iron mordants. About 20 per cent. of alizarin is required for a full shade.

Other Mordant Dyes.—The following are the names of some of the dyes which are dyed with mordants and are often termed alizarin dyes, although they are by no means all of them derivatives of alizarin: Alizarin bordeaux, Alizarin maroon, Alizarin orange, Resoflavin, Alizarin yellow, Galloflavin, Anthracene brown, Alizarin green, Emeraldol, Anthraquinone green, Coerulein, Alizarin blue, Brilliant alizarin blue, Alizarin indigo blue, Alizarin sky blue, Cyananthrol, Anthraquinone blue, Gallocyanine, Gallazine, Phenocyanine, Crumpsall fast blue, Alizarin cyanine, Alizarin cyclamin, Alizarin heliotrope, Anthraquinone violet, Anthracene violet, Alizarin black (see pp. 451-454).

In wool dyeing the order of operations is often inverted, *i.e.*, the wool is first treated ("stuffed") with the dye and then saddened with the mordant. This procedure is particularly suitable for a class of dyes of a strongly acid nature known as **acid chrome colours** which have recently been placed on the market. In this case both operations are carried out in the same vessel (single bath process). The dye is first practically exhausted from the bath, and then ½-2 per cent. of bichromate, according to the depth of shade, is added and dyeing continued at the boil for half an hour to one hour longer, after which the wool is washed and dried. Chromium fluoride may be employed instead of bichromate with those dyestuffs which will not resist the oxidising action of the latter. The following are names under which this class of dyestuff is sold by various makers: **Chrome, Acid anthracene, Acid alizarin, Diamond salicine**, etc.

After-treatment of Cotton with Metallic Salts.—Before leaving the subject of mordant dyes reference must be made to the after-treatment with metallic salts of cotton dyed with the direct and sulphur dyes (p. 545). These salts no doubt act as mordants, although in some cases an oxidising effect exerted by them may also be of importance. Copper sulphate, chromium fluoride, and potassium bichromate are the most important substances employed for this purpose. The following prescriptions will illustrate the process:—

Rinse the cotton well and treat with a cold or tepid solution of 2-4 per cent. of copper sulphate ($CuSO_4$) (the weight of the cotton) for fifteen to thirty minutes; or else with a solution containing 2 per cent. $CuSO_4$, 2 per cent. bichromate, and 3 per cent. acetic acid of 30 per cent. strength under the same conditions; or else boil for half an hour in a bath containing 3-4 per cent. chromium fluoride and 2-3 per cent. acetic acid of 30 per cent. strength.

VAT DYES

Many dyestuffs are converted by reducing agents (*i.e.*, compounds capable of providing nascent hydrogen or removing oxygen) into colourless substances termed leuco compounds, which by oxidation in contact with air pass again into the original dyestuff. Some dyes, on the other hand, undergo so far-reaching decomposition when subjected to reduction that a simple process of oxidation cannot reproduce the original compounds. The leuco compounds are frequently soluble in alkaline solutions, and are taken up readily from these by vegetable as well as by animal fibres. On contact with the air the original dyestuff is reproduced in the fibre in an exceedingly fast form. These facts are made use of in dyeing with certain insoluble dyes known as vat dyes. The dye is brought into solution in the vat, *i.e.*, an alkaline

liquid containing a reducing agent. The material to be dyed is impregnated with the leuco-compound formed, and is then exposed to the air, the dye being thus produced in it.

Indigo.—This, the most important vat dye, which may be considered to be the parent substance of most of the others in common use, is at the present day employed as natural and as artificial indigo. The former is obtained by a process of fermentation (steeping), followed by one of oxidation (beating) from the leaves of various tropical plants. A glucoside which has been named indican by its discoverer, Schunck, is thus decomposed, yielding glucose and the leuco compound indigo white, which latter is converted into indigo by oxidation. Natural indigo usually contains quantities of the pure dyestuff indigotin, varying between 30 and 70 per cent. according to the source from which it has been obtained; in addition there may be in it quantities varying between 2 and 10 per cent. of the purple dyestuff indirubin, while the remainder is made up of more or less inert impurities.

The glucoside indican is also contained in woad, a substance that is still employed as an addition to the fermentation vats used in wool dyeing.

Artificial indigo is manufactured chemically from the products of coal-tar distillation. It is met with in commerce as a powder consisting of almost pure indigotin, as a paste containing about 20 per cent. of the same substance, and in various other forms. It is also sold as "indigo vat," a substance containing about 60 per cent. of the leuco compound indigo white (see p. 458).

As already explained the indigo vat contains essentially a reducing agent and an alkaline substance which dissolves the indigo white formed. The latter is either lime, soda, or ammonia, the former may consist of a large variety of substances. Brief reference shall here be made to the hydrosulphite vats, the zinc and lime vat, the copperas vat, and the fermentation vats.

The sodium hydrosulphite employed in the first-named vats is either prepared by the dyer himself by the action of zinc dust on sodium hydrogen sulphite, or may be obtained commercially at the present day in the form of a dry powder. Either soda, lime, or ammonia may be employed as the alkali of the vat. The vats are usually worked cold for cotton, and at a temperature of about 50° for wool. In the latter case the amount of hydrosulphite is greater, and the amount of alkali smaller, than in the former. A stock or standard vat is always prepared apart from the actual dyeing vat.

The following may be taken as an example of a hydrosulphite-soda vat for **cotton**, prepared with zinc and sodium bisulphite. Volume of dye vat, 1,000 l. A solution is prepared by mixing 15 l. bisulphite solution (sp. gr. 1.28) in small portions with 1.5 kg. zinc dust and letting the mixture stand for a short time with occasional stirring until the sediment is pale grey in colour. A suspension of 15 kg. of 20 per cent. indigo pure paste (equivalent to about 5 kg. very finely ground natural indigo) in about 15 l. of caustic soda solution (sp. gr. 1.38) is then prepared and the first liquid added to the second. The mixture is then maintained at a temperature of about 50° C. during half an hour or one hour. When reduction is complete the stock liquor will have turned yellow. The dye vat (1,000 l.) is prepared with a mixture of 10 l. bisulphite (sp. gr. 1.28) and 1 kg. zinc dust added as above in small portions with stirring. After a short time as much stock liquor as necessary (according to depth of shade desired) is added and the vat stirred well. It is ready for use as soon as it has become clear and yellowish green. The vat may be used continuously and fed with stock liquor and bisulphite-zinc-soda mixture to keep it up to strength.

For **wool** a corresponding hydrosulphite-lime vat may be made up by using, in the place of the quantities given above, the following: For the stock liquors 12 l. bisulphite solution, 1½ kg. zinc dust, 10 kg. indigo paste, 10 l. 20 per cent. milk of lime prepared by slaking 2 kg. quicklime in place of the soda solution; for the dye vat, ¾ l. bisulphite solution, 0.2 kg. zinc dust. As already mentioned, the wool is dyed at about 50°, and after dyeing must be passed through very dilute sulphuric acid solution (0.1 per cent.) to remove the lime and then be rinsed.

The following may be taken as an example of a vat for **cotton** in which commercial sodium hydrosulphite is employed.

The volume of the dye vat is 1,000 l. A stock liquor is prepared by stirring together well 15 l. 20 per cent. indigo paste (equivalent to about 3⅛ kg. very finely ground natural indigo), 20 l. water, and 1¾ kg. hydrosulphite powder. To this, after ten minutes, is added 6 l. caustic soda solution (sp. gr. 1.39), and the whole is heated to 60° C. until reduction is complete.

ascertained by dipping a piece of glass into the liquor. The glass and the drops from it should be clear yellow in colour, and the liquor should oxidise in about half a minute. The dye vat is set with 50 g. hydrosulphite to remove dissolved oxygen from the water, and after stirring, the whole or part of the stock solution is added and the vat stirred up once more.

For **wool**, the quantities for the stock solution are 10 kg. indigo paste, 10 l. cold water, 2 kg. hydrosulphite powder, and 2 l. caustic soda solution (sp. gr. 1.38). It is recommended to make the dye vat up with 50 g. hydrosulphite, about ½ l. ammonia, and 3½ l. of a 10 per cent. glue solution per 1,000 l. and then to add a portion of the above stock liquor. Dyeing takes place at about 50° C. The vat is used continuously and made up to strength from time to time.

The Zinc-Lime Vat.—In this vat, which is extensively used for cotton, the indigo is reduced by nascent hydrogen produced by the action of zinc dust upon lime solution. It is best to prepare a stock solution of reduced indigo.

The following prescription may serve as an example for the preparation of a vat of 1,000 l. A stock solution is prepared by mixing 10 kg. 20 per cent. indigo paste equivalent to about 3½ natural indigo) with 1½ kg. zinc dust made into a paste with 20 l. of water of 50°-60° C. To this is added 1 kg. quicklime which has been previously slaked to a uniform paste. The mixture is made up with hot water to 80 l., and maintained for three to five hours at a temperature of 50°-60° C., with occasional stirring. It should then be pure yellow and ready for use. The vat is set with 250 g. zinc dust and 1 kg. lime slaked to a thin cream, stirred up and allowed to stand for some time. The liquor or part of it is then poured in, the vat stirred and allowed to settle. It is then ready for use. A certain amount of sediment is formed; this may trap a small amount of indigo, producing loss, and may also lead to uneven dyeing if proper attention is not paid. These disadvantages, however, are only slight with this vat, being much less serious than in the following one.

The Copperas Vat.—This is one of the oldest vats employed in the dyeing of cotton. The ingredients used are lime and ferrous sulphate. Ferrous hydroxide is produced which is converted into ferric hydroxide by the indigo contained in the vat, and thus acts as a reducing agent.

The following prescription for a vat of 1,000 l. of medium strength will illustrate the process. A stock vat of 200 l. containing 10 kg. 20 per cent. indigo paste, 12½ kg. quicklime, and 10 kg. copperas is made up, and allowed to stand for four to six hours with occasional stirring. As soon as it has assumed a yellow colour, it is poured into the dye vat which has been about three-quarters filled with water. The latter is stirred up and dyeing commenced after it has settled completely. This vat is easy to set, but the large sediment referred to above is a grave disadvantage, and renders it unsuitable for continuous dyeing.

Fermentation Vats for Wool.—In the fermentation vats various organic substances are allowed to ferment. Glucose is thus produced which acts as a reducing agent upon the indigo contained in the alkaline liquor. The sugar is formed by the latter, first to lactic and then to butyric acid. A great deal of practical experience is necessary to work a fermentation vat properly, and all that can be attempted here is to give a very rough sketch of the most important fermentation vat for wool, *i.e.*, the woad vat.

A vat containing 15,000 l. is often employed. It is filled with water and heated to 65° C., 2 kg. of woad are introduced, and after stirring left overnight. The next morning 20 kg. very finely ground indigo, 20 kg. bran, 7 kg. madder, and 12 kg. lime are added. The whole is stirred up three times a day with the addition of 1-2 kg. of lime each time, the temperature being maintained at about 60°. After a few days the liquor should show a yellowish colour, and on gently stirring it, blue streaks should make their appearance along with a coppery scum or flurry. Before dyeing the wool must be very thoroughly scoured and the soap removed. A trammel net is placed in the vat to preserve the wool from contact with the sediment. After dyeing, the wool is thoroughly cleansed with soap and fuller's earth in order to remove all the loosely adhering indigo which would otherwise show the objectionable property of rubbing when in use.

Silk is not very frequently dyed with indigo. The vats must be kept less strongly alkaline than for cotton and are worked in the cold. In applying the hydrosulphite vats, the material is always worked in the liquor for various periods of time—cotton yarn, three or four minutes; for calico, ten to thirty minutes; and for woollen cloth half an hour to two hours or more. On coming out of the vat the goods, which show a greenish yellow colour, are squeezed or wrung and exposed to the air. The shade quickly passes by oxidation through green to

blue. The operation is then repeated either in a stronger or weaker vat until the desired shade has been attained.

Numerous machines for dyeing with indigo, some of which have been referred to in the chapter on appliances for dyeing, have been designed for use with the various forms of textile goods. They are designed to carry out the operations of steeping and oxidising the goods in a continuous manner.

Other Vat Dyes.—During the last ten years a considerable number of new vat dyes have been put on the market, most of which are distinguished by their great fastness to light and other influences, and which promise to become of the very greatest importance in the future. They are mostly employed in conjunction with the hydrosulphite vats. The following are the more important classes:—

The Thioindigo Class is of great theoretical interest. They are chemically derived from indigo by replacing NH groups by S atoms. The following are some of the more important dyes of this series: Thioindigo red, Thioindigo scarlet, Thioindigo violet (Kalle), Vat red B (B.A.S.F.), Helindone red 3B, Helindone orange, Helindone yellow 3G, Helindone scarlet S, Helindone fast scarlet, and Helindone brown G (M.L.B.). All these dyes may be employed for cotton and wool (see p.

The Ciba Colours (S.C.I.B.) are apparently either brominated derivatives or derivatives of the thioindigo class. Most of them may be applied equally well to animal and vegetable fibres. The more important ones are the indigos put on the market by M.L.B. and the B.A.S.F. Ciba blue B and (S.C.I.B.), Ciba heliotrope, Ciba Bordeaux B, Ciba red G, Ciba scarlet G, Ciba G and B, Ciba green G, and Ciba violets (see pp. 461, 466).

The Indanthrene, Algole (B.A.S.F.) and **Leucole** (Bayer) and **Ci** (S.C.I.B.) colours have no chemical connection with indigo, but are mostly to anthraquinone. They require the addition of a large amount of alkali hydrosulphite vat, and are therefore unsuited for use with the animal fibre following may be mentioned: Indanthrene yellows (flavanthrene), orange, reds, Rufanthrene browns (fascanthrene), Indanthrene claret, Indanthrene Indanthrene violets (violanthrene), Indanthrene grey, Indanthrene maroon anthrene), Indanthrene brown, Indanthrene green (viridanthrene), Indanthrene (melanthrene), Algole yellows, orange, scarlet, reds, grey, blues, pink, Bordeaux, Cibanone yellow, orange, browns, and blacks (see p. 454).

Certain of the sulphide dyes, such as kryogene black, may also be dy vat, and should, therefore, be mentioned here (see pp. 458, 478).

DYESTUFFS PRODUCED BY CHEMICAL MEANS THE FIBRE

Aniline Black

This dyestuff, which is of the greatest importance in cotton dyeing, is al produced on the fibre as a perfectly insoluble substance by the oxidation aniline salt. When an acid solution of aniline is treated with suitable oxidis base undergoes a very complicated series of oxidations and polymerisati considerable number of intermediate products is produced and ultimately a blac soluble substance of very high molecular weight "aniline black," is formed (p.

This substance appears to exist in two states of oxidation or polymerisation first has the property of acquiring a greenish tint under the action of sulphurous the second more highly oxidised, or perhaps only more highly polymerised pr does not exhibit this reaction; and it is this form which the dyer must a producing, if the dyed fabric is not to turn green during use. The cotton is, ther usually subjected to an after-treatment in a hot chrome bath in order to c

[redacted]he whole of the first into the second form of aniline black. The oxidiser employed [redacted]or oxidising the aniline salt in the first instance may be sodium (or potassium) [redacted]te; potassium ferricyanide (red prussiate of potash), or what comes to the [redacted]ning, a mixture of sodium chlorate and potassium ferrocyanide; or lastly, [redacted]chlorate. The last-named substance requires the intervention of a catalyst [redacted]r of oxygen, and as such, a salt of copper, iron, or vanadium may be employed. [redacted]e substances are sometimes also added to chromate solutions to accelerate [redacted]n. The oxidation takes place in the fibre, with a suitable velocity at [redacted]tures at or about 45° C., and the following processes, producing what are (1) dyed blacks, (2) aged blacks, and (3) steam blacks, are in use. In the [redacted]ed process the material (say 100 kg.) is worked in a dye bath of 2,000 l. [redacted]g, say, 13 kg. aniline salt, 20 kg. hydrochloric acid (sp. gr. 1.171), 14 kg. [redacted]te, first in the cold for an hour. The temperature of the bath is then [redacted]70°-80° C. and the cotton is worked for another half hour, during which [redacted]k is developed. It is then rinsed and soaped well, hydro-extracted, and [redacted]he disadvantage of this process is that the dyestuff is not held well by the [redacted]ubs badly. The second or **ageing process** is the one most frequently [redacted]. It differs from the first in making use of a much more concentrated [redacted]d in the fact that the oxidation is not accomplished in the liquor itself, [redacted]e fabric is removed from it, dried, and then aged, that is, subjected to [redacted]m atmosphere which develops the black. During the process of ageing [redacted]ntities of hydrochloric acid and oxides of chlorine are liberated from the [redacted]ne hydrochloride, and there is thus always a considerable risk of tendering the [redacted]ic if the temperature is not carefully regulated and the acid efficiently removed [redacted]he current of air. An addition of aluminium acetate is recommended to [redacted]ralise the mineral acid given off.

[redacted]e following prescription for yarn by K. Oehler will give an idea of the process. The cotton [redacted]thoroughly boiled out with soda, well rinsed, hydro extracted, and stretched. 25 kg. are then [redacted]for half an hour in a padding liquor made up to 500 l., after pouring together the following [redacted]: 60 kg. aniline salt dissolved in 320 l., 2.75 kg. bluestone (copper sulphate) dissolved [redacted]18.8 kg. sodium chlorate dissolved in 37 l., 2 kg. ammonium chloride dissolved in 12 l., [redacted]of an aluminium acetate solution (sp. gr. 1.075). The yarn is then wrung or hydro- [redacted]lightly until it retains about its own weight of liquor. It is then well stretched, placed [redacted]n laths which have been wiped over with the padding liquor, dried, and aged. The drying [redacted]g are conveniently carried out in the same chamber; the drying takes about four to six [redacted]ageing proper is begun by carefully admitting steam until the dry bulb thermometer registers [redacted]e wet bulb 30° C. The ageing chamber is fitted with a powerful fan at the top, which [redacted]air through the bottom; this air is heated by means of pipes which also serve for the intro- [redacted]of steam. While in the ager the yarn is turned every two hours; the ageing occupies about [redacted]ght hours. After leaving the ager the yarn is chromed by turning quickly for ten to fifteen [redacted]at 75°-80° C. in a bath containing 3 kg. bichromate and 0.75 kg. sulphuric acid per 1,000 l. [redacted]thoroughly rinsed, soaped, rinsed again, and dried.

[redacted]process which bids fair to become of the very greatest importance in the [redacted]tion of aged blacks has been recently patented by A. G. Green. In it the [redacted]idising agent employed is atmospheric air. This is accomplished by making [redacted]he observation that a small quantity of a diamine, *e.g.*, paraphenylenediamine, [redacted]utes, when associated with a copper salt, a catalytic system by means of [redacted]aniline can be readily oxidised by air alone.

[redacted]the **Steamed Blacks** the oxidising substance is essentially potassium [redacted]anide. The cotton may be padded with a liquor containing 75 kg. aniline salt, [redacted]sodium chlorate, 40 kg. yellow prussiate of potash per 1,000 litres; it is then [redacted]at a temperature not exceeding 50° C., and the black then developed by steam [redacted]w minutes in a suitable ager.

[redacted]advantage of this process over the ageing method lies in its rapidity and in the fact that [redacted]ittle risk of tendering, as very little mineral acid is given off in the presence of the potassium [redacted]ide; its disadvantage lies in the greater expense.

[redacted]ious other bases besides aniline may be oxidised on the fibre to produce [redacted]blacks or other dyes. Thus a black is obtained from *p*-amidodiphenylamine [redacted]rown from *p*-phenylenediamine.

Ice Colour (see pp. 442, 450, 545)

The ice colours are employed in cotton dyeing. They belong to the insoluble azo dyes, and are produced on the fibre itself (p. 545) by the same c processes by means of which azo dyes are manufactured in the colour works

As is well known (see p. 441), the following operations are carried out in the pro azo dyes: First an aromatic base is diazotised by dissolving it in an excess of acid, cooling th with ice, and adding to it a solution of sodium nitrite. As soon as the starch iodide test s the nitrous acid is no longer being used up in the chemical reaction, the diazotised solution into an alkaline solution of a phenol, or it is allowed to act on a slightly acid, neutral, c solution of an aromatic base (see pp. 442, 450).

In the production of azo colours in the cotton fibre, the latter is impregnated first with the alkaline solution of the phenol. β-naphthol is stance almost exclusively employed for this purpose. The cotton is padded quantities at a time in a strong solution containing the naphthol and cau and some turkey-red oil. The material is then hydro-extracted and drie in a well-ventilated room at medium temperature. After it has been well cooled it is ready to be developed by introducing it into tion of the diazotised base. Various substances producing different s diazotised paranitraniline, chloranisidine, alphanaphthylamine, and o bodies are in use for this purpose, but the first-named is the easie and the most frequently employed. The dye obtained is known unde of paranitraniline red. The diazotisation is in this case carried out together the very carefully weighed out chemicals, and should take pla temperature (say 10° C.). The temperature should never rise higher 15°. Since a strongly acid solution, like the one obtained in this op not couple with a phenol, it becomes necessary to make it either neutr acid by the addition of caustic soda or sodium acetate respectively. Th must not be made alkaline since diazo solutions are unstable in this conditio

It is thus obvious that great care must be taken by the dyer in weighing out his chemic a rule, his weighings alone are relied upon to give the right proportions, and are not ch special tests. Compared with other diazo salts, those derived from *p*-nitraniline are exc stable, and it is a great advantage to the dyer that these diazo-salts may be obtained com ready made. They are sold mixed with indifferent substances, such as aluminium or sodium to render them non-explosive, and are found on the market under the names of **Nitrazol C** and **Azophore red** (M.L.B.). Another product of a similar nature is **nitrosamine red** (B which represents *p*-nitrophenylnitrosamine sodium (antidiazo-*p*-nitrobenzene sodium). This s is converted into *p*-nitrodiazobenzene chloride by simply adding hydrochloric acid in the co solution. It is then allowed to stand for half an hour, and on the addition of sodium ace ready to be employed in the process of developing.

In conjunction with the ice colours the two processes known respecti "diazotising and developing" and as "coupling" must be considered here. processes are employed extensively as methods of after-treatment for the cotton colours. The last-named is also applied occasionally to cotton, dyed w sulphur colours.

The majority of direct cotton colours belong to the class of amido bodies, to the class of phenols. The former may be subjected to both methods of treatment under consideration, the latter only to the second. In the first-n process the dye is diazotised on the fibre, and the compound formed, coupled the solution of a suitable developer, *i.e.*, either an amido body or a phenol. second process the dyed fabric is treated directly with the solution of a diaz base, or of one of the commercial diazo bodies mentioned above.

The following prescriptions will illustrate the methods:—

Diazotising and Developing.—Wash the material well after dyeing with the direc colour and then work for fifteen to thirty minutes cold in a dye bath charged with 1-3 per cent nitrite and 5-10 per cent. spirits of salt (hydrochloric acid). The cotton is lightly rinsed an without delay or unnecessary exposure to light and air into the cold developing bath in w worked for fifteen to thirty minutes. It is then washed and dried. Of the numerous de

which may be employed, the following may be mentioned: Phenol, Resorcinol, Alpha and Beta Naphthol, Para-amidodiphenylamine, etc. The first four are dissolved in caustic soda, the last named in the minimum amount of hydrochloric acid.

Prescription for "coupling" for 100 kg. cotton: Make 0.5-0.6 kg. of paranitraniline into a paste with an equal quantity of hot water, then add 1-1½ l. of cold water and 1.5 kg. hydrochloric acid (sp. gr. 1.1[illegible]) and let stand until the mixture has cooled to 20° C. Then stir in 2 kg. broken ice and add all at once ½ kg. solid sodium nitrite, taking care that the temperature does not rise above 10° C. Pour this solution into the coupling bath which has been filled with cold water, and add a solution of 1½ kg. crystallised sodium acetate. Enter the dyed and rinsed cotton, work for about thirty minutes, rinse, and dry.

Mineral Colours

Although largely displaced by modern organic dyes, yet a few mineral colours have still retained a certain degree of importance in cotton dyeing. They are always produced in the fibre itself as insoluble pigments from substances which are not dyes.

Chrome Yellow and Orange.—These substances consist of ordinary and basic lead chromates respectively (see p. 500). Chrome yellow may be produced by fixing lead oxide on the fibres, and then passing it through a hot dilute solution of potassium dichromate. The first-named operation is carried out by impregnating the material with a soluble lead salt, and then passing it through dilute lime water. Another method of procedure consists in impregnating the cotton first with an alkaline lead solution containing, say, $\frac{1}{10}$ per cent. lead acetate and 0.8 per cent. caustic soda (on the water), and then passing through an acidified solution of bichromate containing, say, 1 per cent. of bichromate and ½ per cent. sulphuric acid.

Chrome orange is obtained by dyeing the cotton first with chrome yellow, washing, and then working in boiling clear dilute lime water until the desired shade has been obtained.

Manganese Brown is obtained by impregnating cotton with a solution of manganous chloride, and then passing it through a hot solution of caustic soda (sp. gr. 1.01) free from carbonate. Colourless manganous hydroxide is thus precipitated, which is converted into the brown higher oxides of manganese by exposure to air and a passage through a weak solution of bleaching powder.

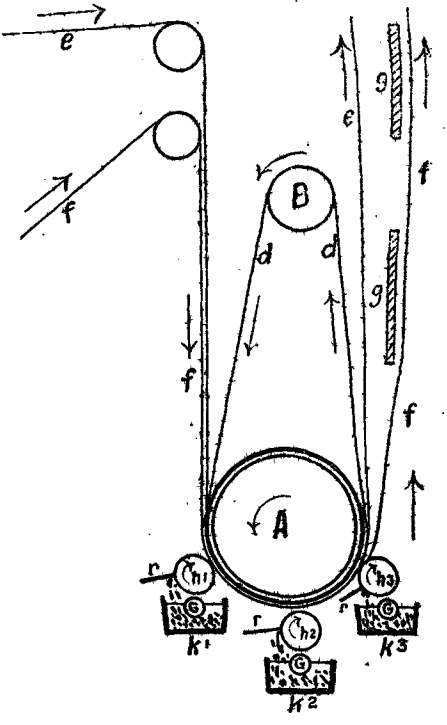


FIG. 223.—Section of Three-Colour Printing Machine.

Mineral Khaki may be obtained by impregnating the cotton with a mixture of ferrous and chromic acetates. After drying, it is then steamed in a rapid ager which leads to the production of a mixture of basic ferric and chromic acetates on the fibre. These are further fixed by passing the goods through a boiling solution containing a mixture of sodium carbonate and sodium hydroxide.

Iron Buff consists of ferric hydroxide, and may be dyed on cotton by the same method employed for manganese brown, only substituting green vitriol for manganous chloride. It may also be obtained by successive treatment with a ferric salt and caustic soda or lime.

Prussian Blue may be obtained on cotton by first dyeing it an iron buff, and then working it in cold solution of potassium ferrocyanide containing, say, 2 per cent. ferrocyanide, 1 per cent. sulphuric acid, on volume of bath (see p. 502). Prussian blue is frequently employed as a groundwork in the dyeing of heavy blacks on silk.

Prussian blue is also dyed on wool. It is usually obtained by the oxidation at a high temperature of hydroferro or hydroferri cyanic acid liberated respectively from potassium ferro, or potassium ferri cyanide. An addition of a stannous mordant improves the colour.

The wool may be introduced into a cold bath containing 10 per cent. red prussiate of potash and

20 per cent. sulphuric acid (on weight of wool). The temperature is gradually raised to boiling and maintained thus for about half an hour or more. About 1-2 per cent. of stannous chloride may be added towards the end of the operation.

COLOUR PRINTING OF CALICO

In colour printing the dyes are confined to certain portions of the fabric, being printed on by special rollers and prevented from spreading to neighbouring parts by the addition of thickening agents to the dye, such as starch paste, dextrine, gum arabic, gum tragacanth, albumen, casein, and similar substances. The dyes are usually applied in a water-soluble form, as in dyeing, and are fixed in the fibres by

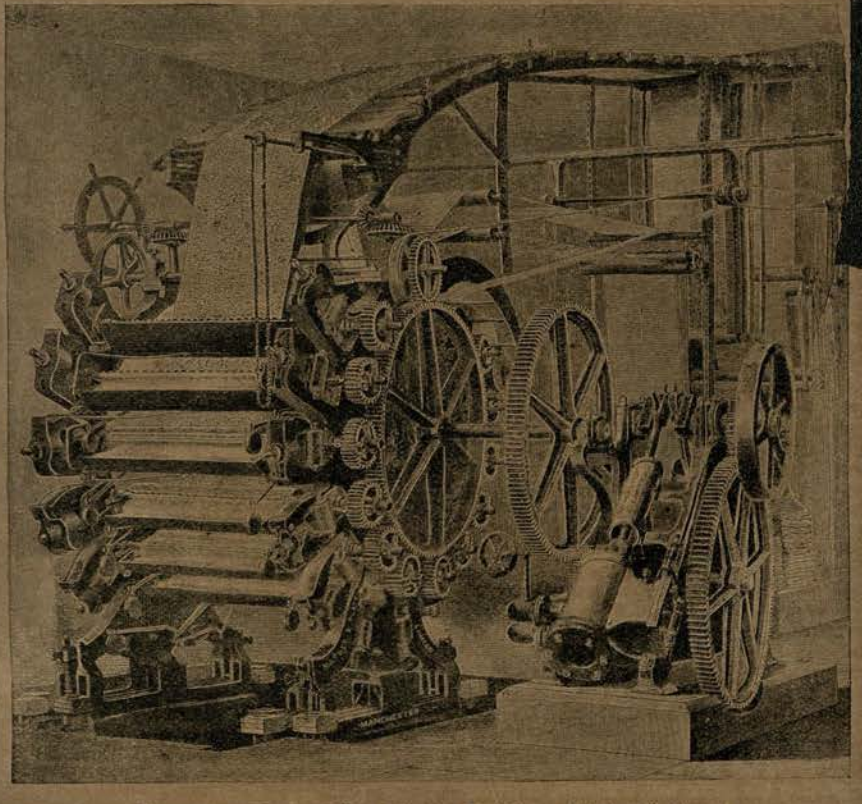


FIG. 224.—Twelve-Colour Printing Machine. (Mather & Platt.)

suitable mordants followed by steaming in chambers. Sometimes insoluble colouring matters are fixed on with adhesives—usually blood albumen (see p. 597); on steaming the albumen coagulates and fixes the dye in an insoluble wash-fast form on the fibre. Such colours are known as "albumen colours," and comprise insoluble mineral colouring matters, such as ultramarine, Guignet's green, chrome yellow, cinnabar, zinc white, etc.

The printing is carried out by means of hollow copper rollers, usually 1-1½ yds. long by 4-6 in. in diameter, provided with a steel core. The patterns are etched on the copper by means of acid in the usual way, the colour collecting in the hollows of the roller and being pressed on to the cloth as it passes under it. Each colour has its own roller with its own special pattern. Printing machines are now made in which one to fourteen colours are printed on the cloth in a single operation, usually

on one side only of the fabric, but in duplex machines the patterns, exactly corresponding, are printed on both sides.

Fig. 223 shows the principle of a printing machine (three-colour). A is a large hollow iron roller a yard or more in diameter, covered with a thin layer of cloth; over this and over a smaller roller B runs the endless rubber cloth *d*; over this runs the cloth *f* which is to be printed, together with a supporting cloth *e*; k_1, k_2, k_3 are the printing rollers, which take up colours from the rotating rollers placed in the colour cisterns k_1, k_2, k_3; any excess of colour is scraped off the printing rollers by the special knife edges *r*, *r*, *r* pressing against them. The cloth *f* as it passes between each printing roll and the large iron cylinder has a coloured pattern printed on it. The cloth then passes away and is immediately dried (to prevent the colours from running) by passing over hot plates *g*, *g* or into a hot air drying chamber. The colours are then fixed by steaming in a special chamber.

FINISHING

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The printed cotton cloth is always "finished" in order to weight it and give it a better appearance. The finishing materials consist of starch paste ("size"), mixed with such mineral salts as kaolin, gypsum, barium sulphate, magnesium sulphate, chalk, etc. If a highly glazed surface is required a little paraffin or soap is added. To obtain a pure white, and correct any yellowish tinge, it is usual to mix in ultramarine or other suitable colouring matter in small amount. A "soft" touch is imparted to the cloth by the presence of magnesium chloride, calcium chloride, or glycerol, which are all hygroscopic. The finishing paste is evenly spread over the cloth by means of "sizing" machines, and dried by passing the cloth over hot drums. Shrinkage is avoided by drying in a stretched condition in special frames. The goods are then "calendered" by passing between hot smooth steel rollers, whereby they acquire a fine glaze. A fine silky appearance may be given to cotton goods by stamping or subjecting to very great pressure between special rolls (satin). Woollen goods (*e.g.*, flannel) may be given a rough hairy appearance by passing over rotating cylinders provided with fine steel points.

Fig. 225.—Fourteen-Colour Printing Machine. (Mather & Platt.)

Cloth is made by mechanically working woollen goods in soap solution, whereby the fibres become more or less matted

together ("milling" or "fulling"). For particulars of this and other special processes works on cloth-making must be consulted.

Acknowledgments.—The author wishes to express his thanks to the following firms who supplied him with many samples of dyed material and with much information regarding the newest processes of dyeing: Read Holliday & Sons, Ltd.; Cassella & Co., The Badische Aniline u. Soda Fabrik, Meister Lucius & Brüning, Kalle & Co., Farbenfabrik F. Bayer & Co.

SECTION XIX

The Leather and Tanning Industry

THE LEATHER AND TANNING INDUSTRY

By D. J. Law, B.Sc., F.I.C.

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In the following pages the writer has endeavoured to give, as far as possible, a review of the processes through which the raw hide or skin passes during its conversion into leather. From the exigencies of space it is evident that the merest outline only can be given of some of the more typical methods, since no two factories follow exactly the same method of procedure, and the possible modifications of the standard processes are endless.

A short account of analytical processes is given in those cases only in which they differ from, or are not included in, the ordinary methods of quantitative analysis.

The writer wishes to acknowledge the help received from information contained in Professor Procter's "Principles of Leather Manufacture," also his thanks to Mr J. T. Wood for reading the proofs.

The illustrations are from blocks kindly supplied by Messrs T. Haley & Co., Bramley, Leeds.

The magnitude of the leather industry may be gauged by the following statistics:—

Imported into the United Kingdom.

	1906.	1910.	Value in 1910.
Undressed leather	925,252 cwt.	904,205 cwt.	£5,051,827
Dressed leather	360,144 ,,	271,366 ,,	4,336,677
Varnished, japanned, or enamelled leather	6,541 ,,	7,095 ,,	241,167
Leather machinery belting	4,457 ,,	3,069 ,,	38,297
Leather boots and shoes	211,501 doz. pairs	168,236 doz. pairs	673,674
Leather gloves	1,513,888 ,,	1,367,498 ,,	1,561,753
Other manufactured leather goods	...	...	595,020
Dry raw hides	484,218 cwt.	516,896 cwt.	1,855,804
Wet raw hides	533,678 ,,	764,155 ,,	2,417,028
Total	...	...	£16,771,247

EXPORTED FROM THE UNITED KINGDOM.

	1910.	Value.
Undressed leather	105,373 cwt.	£885,848
Dressed leather	113,919 ,,	1,892,569
Varnished, japanned, or enamelled leather	1,262 ,,	36,423
Leather machinery belting	39,448 ,,	515,450
Leather boots	1,086,638 doz. pairs	3,029,892
Leather gloves	228,870 ,,	344,119
Other manufactured leather goods	...	527,887
Raw hides	196,962 cwt.	552,021
Total	...	£7,784,209

The following statistics refer to the United States :—

IMPORTED INTO THE UNITED STATES.

	1910.	Value in 1910.
Patent, japanned, or varnished leather	1,230 cwt.	$237,000
Skins for morocco	...	1,994,000
Upper, dressed and finished	..	972,000
Calf skins, tanned	...	270,000
Chamois and other	...	1,356,000
All other	...	2,779,000
Manufactured leather, gloves	...	7,782,000
,, ,, all other	...	1,476,000
Hides (cattle, goat, sheep, etc.)	5,434,000 cwt.	112,247,000

EXPORTED FROM THE UNITED STATES.

	1910.	Value in 1910.
Sole leather	342,200 cwt.	$8,308,000
Upper leather	...	15,988,000
Manufactured leather—		
Boots and shoes	7,257,000 pairs.	12,409,000
Harness and saddles	...	842,000
All other	...	1,982,000
Hides and skins	130,700 cwt.	1,738,000

(For **Tanning Materials** see p. 575.)

The object of leather manufacture, as defined by Professor Procter, is the conversion of the "putrescible animal skin into a material which is permanent and not readily subject to decay, while retaining sufficient softness and flexibility for the purposes for which it is intended."

Theory of the Tanning Process

The nature of the change which the raw hide undergoes during the process of its conversion into leather is not well understood. The issue is complicated by the fact that the raw materials (including the gelatigenous hide fibre, the vegetable tannins.

and the basic mineral salts used in tanning) are "colloidal," and follow the laws of colloidal chemistry, a branch of the science neglected till very recently, but in the investigation of which great strides have been made during late years. The main point at issue is whether the process is to be looked upon as a chemical combination between gelatine and tannin, or a mutual co-precipitation of colloids.

Sir Humphry Davy* in 1803 precipitated solutions of gelatine by tannin and found that the quantity of precipitate produced is not always exactly proportional to the amount of gelatine and tannin in the solutions used, but is influenced by the concentration of the solutions. J. T. Wood,† working on similar lines, considers the precipitation neither purely chemical since the gelatine-tannin compound is not of constant composition, nor purely physical since the precipitation does not obey the solution laws, which require the concentration of the tannin in the solution and in the precipitate to maintain a constant ratio. The physical theory was first proposed by Knapp in 1858, who was also the first to recognise the fact that the conversion of skin into leather consisted of the drying of the fibres without allowing them to adhere. Stiasny‡ thinks that the hide first adsorbs the tannin from its colloidal solution, and then the tannin undergoes a further change under the catalytic action of the hide fibre. He explains the increase of insoluble matter which goes on after the leather is tanned as due to further chemical changes in which oxidation plays a large part. Fabrion, from the result of a large number of experiments in chamois, aldehyde, vegetable and mineral tannages, thinks that leather consists of a salt of the oxidised hide fibre.§ Though holding that the true tanning process is purely chemical, he recognises that the simultaneous physical processes of capillarity, diffusion, and adsorption are indispensable. He points out‖ that the inner parts of the hide are accessible to crystalloids only and differentiates between true tannages in which the condensation takes place directly between the tanning agent and the hide fibre, and pseudo-tannages in which the tanning agent undergoes some change before acting as such.

Dr J. von Schroeder¶ considers tanning primarily an adsorption process, and that the adsorption compound undergoes a change in the course of time, resulting in a more stable union of the tannin with the hide fibre. He finds that tannin is not taken up by hide powder from alcoholic solution, and from this emphasises the importance of the action of water in swelling the fibre and thus rendering it in a condition to be precipitated by tannin. The final solution of the problem will probably lie in regarding the process as the effect of both chemical and physical forces acting in conjunction.

The Raw Skin

The structure of the skin of all the mammalia is essentially the same though differing greatly in thickness and texture according to its origin. So far as leather-making is concerned skin may be taken as consisting of two layers, the outer constituting the **epidermis** or **epithelium** (E, Fig. 226), and the inner the **corium** or **dermis** (C), the true skin.

The epidermis, which is completely removed in the operations of liming, etc., before tanning, is very thin in comparison with the true skin. Its inner surface consists of a mucous layer, the "*rete malpighi*," which is in contact with the corium and is made up of soft cells, of which the wall is composed of keratin. These cells in the living organism are continually being forced toward the outer surface, their place being taken by new ones. As they approach the surface they become flattened and finally dry, and forming a horny layer, drop off. The epidermis is thus in a continual state of renewal. Separating the **epidermis** from the **corium** is the **hyaline layer**. This constitutes the extremely thin "grain" surface of the tanned leather and is of a different structure from the rest of the corium, which is apparent from the different colour of the leather in any place from which it has been removed before tanning. The hair (H, Fig. 226) and sweat (S) and fat-glands (T) are developed from the epidermal layer, and the hair in the early stages of its growth grows backwards into the corium, whence it derives its nourishment.

The structure of the **corium** or true skin differs essentially from that of the epidermis, and consists of bundles of interlacing fibres which are themselves composed of fibrils of extreme fineness cemented together by a somewhat more soluble substance. The texture is looser in the centre of the skin, especially so in sheep skins of which the grain and flesh may frequently be torn apart. The structure becomes much more compact at the surface just below the epidermis and constitutes the *pons papillaris* or "grain" and contains the fat-glands. The appearance of this surface and the arrangement of the hair-openings is frequently the only evidence from which the origin of the skin, after tanning, can be deduced. The dermis also contains fibres of another character termed the "elastic fibres,"

* *Phil. Trans.*, 1803, 233.
† *Journ. Soc. Chem. Ind.*, 1908, 384.
‡ *Zeitsch. f. Chemie und Industrie der Kolloide*, 1908, vol. 9.
§ *Zeit. für Angew. Chemie*, 1909, 2083-97, 2135-44, 2187-94.
‖ *Collegium*, 1910, 240-259.
¶ "Zur Kentniss des Gerbprozesses" (Kolloidchemischen Beiheften), 1909.

FIG. 226.—Vertical Section through Skin.

these are yellow in colour and differ greatly from the rest of the skin substance in their resistance to dilute acid, which causes the fibres of the connective tissue to swell and become transparent while the yellow fibres are unaffected.

The chemical composition of the white connective tissue corresponds very closely to that of gelatine into which it is converted by boiling with water. Von Schroeder and Paessler give the following figures for the ultimate analysis of purified corium: C 50.2 per cent., H 6.4 per cent., N 17.8 per cent., and O 25.4 per cent.

An important property of gelatine or hide fibre, from the tanner's point of view, is its capacity of combining both with acids and bases, which it does by virtue of the amido and carboxyl groups contained in the molecule. Under the action of dilute alkalis or acids, or by heating under pressure, gelatine is converted into peptones which do not gelatinise on cooling but resemble gelatine in being precipitated by tannin and meta-phosphoric acid. Longer periods of such treatment or raising to higher temperatures result in the final splitting up of the molecule into nitrogen, ammonia, water, and carbonic acid, with amido acids as intermediate products. Similar products are the result of the action upon gelatine of gastric and pancreatic juice and enzymes secreted during the growth of bacteria. The interfibrillar substance of the raw hide consists of corium which differs from the connective tissue in some respects, notably in its greater susceptibility to solution by dilute solutions of caustic alkali. Procter, however, considers it probably merely an impure degradation product of hide fibre or gelatine.

The epidermis, hair, and glands belong, chemically, to the class of "Keratins." They are more readily attacked by caustic alkalis than is the gelatigenous hide fibre, hence the use of lime for the removal of hair and epidermis. They also differ from gelatine in not swelling in cold water, only dissolving in hot water at temperatures above 100° C.

The raw material for the manufacture of leather may be taken as consisting of three classes—hides, kips, and skins.

Hides consist of the skins of oxen, cows, and horses. In addition to the fresh market hides of home origin, sun-dried hides are imported from the Argentine, Uruguay, China, and Africa, and from America, Europe, and the Colonies in the salted condition.

Kips are the skins of small native cattle, imported mostly from India either in the dried or dry-salted condition, or after a rough and incomplete native tannage.

For the manufacture of the lighter kinds of leather the major part of the raw material consists of the **skins** of calves, sheep, and goats. Skins of deer, pigs, and seals are also used to some extent. The skins of snakes, alligators, and some fish yield a leather which is much used in the manufacture of fancy articles. Much leather is made in Australia from the skins of the kangaroo, wallaby, and other marsupials. Hippopotamus, elephant, and walrus hides are tanned into a very stiff and thick leather used in the "buffing" of cutlery.

Water.—In an industry such as we are dealing with in which such large quantities of water are used, the quality of the water supply is of extreme importance. The presence of a large amount of lime and magnesia compounds results in a great loss of tannin, which is rendered inactive through the formation of an insoluble precipitate. Even in cases where no combination takes place the presence of dissolved salts in water used for leaching tanning materials materially reduces its efficiency.

Eitner* has studied the effect of water, containing various salts in solution, on the raw hide. In his experiments the hide had been unhaired by sweating, and was kept in contact with the solutions for four days at a temperature of 46° F. Water containing lime sulphate and magnesia sulphate had the greatest plumping effect, while the carbonates of lime and magnesia present in the same strength produced a moderate plumping. The chlorides of magnesia and sodium had a repressing action, as hide in these solutions was less plumped than in distilled water. He also found that hide was well plumped in water saturated with CO_2. These results, being obtained with the use of sweated hide, will naturally not hold in the case of a limed hide. Thus a limed hide brought into water containing carbonic acid or bicarbonates will "full" on account of neutralisation of the lime. The precipitation of calcium carbonate in this manner is frequently a source of trouble, as scudding is thereby rendered difficult and the knife is liable to break the grain. The weak acids in the bates and puers will remove lime but not the calcium carbonate, which is dissolved by the drench acids, leaving the skin, however, permanently damaged in those portions in which the "blasting" has occurred.

Iron is especially objectionable if present to any appreciable extent in the water used for preparing goods for tanning, its presence resulting in a bad colour by combination with tannin. Decaying organic matter and the presence of bacteria are objectionable, and a frequent source of danger in the soaks. Where the hardness of the water supply is such as to render its use impossible, one of several methods of softening are employed.

Soaking.—The treatment undergone by the hides or skins previous to entering the limes is modified by the state of the goods or the method of preservation used Hides which have been preserved by the use of salt require more washing than fresh ones, in order, as far as possible, to remove the salt which would otherwise hinder satisfactory plumping in the limes. Dried hides and skins require a comparatively long soaking before the requisite degree of plumpness and flexibility is attained, while with fresh market hides the object of soaking is simply the mechanical removal of blood and dirt.

The use of putrid soaks was formerly much resorted to, but is largely superseded owing to the loss of hide substance thereby incurred, and the danger of destruction of the goods by excessive bacterial action. Softening and cleansing is much hastened by drumming in the tumbler (Fig. 227), through which a stream of water is kept running as the drum revolves. A more violent softening treatment is that of working in the "faller-stocks" (Fig. 228) in which the goods are placed in a wooden or metal box in which two heavy hammers, actuated by pins on the circumference of a revolving wheel, fall alternately.

Mechanical treatment has been rendered unnecessary to a large extent by the addition of various swelling agents in small quantities to the soak water. Solutions of caustic soda (1 : 1,000) or sodium sulphide ($1\frac{1}{2}$-3 : 1,000) as suggested by Eitner

* *Gerber*, iii., 1877, p. 183.

FIG. 227.—Tumbler.

are the most commonly used, swelling being rapidly obtained, and all danger of putrefaction being avoided. Solutions of sulphurous acid and dilute mineral acids are also used.

Depilation

A method of depilation which was practised more generally in earlier times and still to a considerable extent is that by means of "sweating." The hides or skins are hung in a closed chamber in a damp atmosphere and with little or no ventilation. Ammonia is produced in large quantities by bacterial action on the hair roots, and the hair or wool is quickly loosened.

There is always danger of damage to the grain by excessive bacterial action, and the process finds its principal application in the removal of wool from sheep skins where the wool removed is more valuable than the skin. It is also used for the removal of hair from hides for sole leather, but the process was never a success in England, probably on account of bad management. Goods which have been sweated must be brought into a swollen condition before tanning—this is done either by a subsequent treatment with lime or by acid in the earlier liquors.

The general method of unhairing is by the use of lime. This step in the manufacture of leather is the one which has undergone least modification in the light of increasing scientific knowledge.

The reason for this probably lies in the exceeding safeness of the process. The limited solubility of lime (a saturated solution is of about one-twentieth normal strength) imposes a limit on the strength of the alkaline solution, and the tanner can, and always does, use a large excess of lime. The slowness of its action, also, permits of the proper duration in time of liming to be greatly exceeded without material damage to the goods. The removal of hair, although the most apparent of the effects of the liming process, is only one of the results attained by it. The hide substance, as shown above, consists of an agglomeration of fibres which are themselves capable of being split up into bundles of exceedingly fine fibrils. This is actually brought about in a fully limed skin, which, on that account, offers an enormously increased surface to the tanning liquor which coats each fibre with an insoluble and isolating covering. Solution of the interfibrillar substance also takes place in the lime

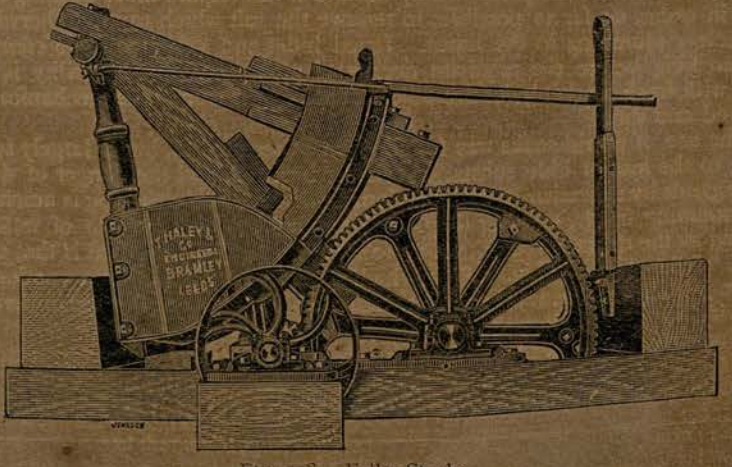

FIG. 228.—Faller-Stocks.

liquors, which are regulated according to the class of goods for which the skin is intended. Thus, this solution of hide substance is reduced to a minimum in the case of hides for sole leather, while, with light skins, in which suppleness and softness are aimed at in the finished article, it is encouraged and carried further in the puer-shop. In the case of skins to be tanned with chrome, which is, in itself, an "empty" tannage, solution of interfibrillar matter is kept at a minimum.

Lime is received at the tanyard in the form of quicklime, CaO, and requires to be slaked before use.

The presence of magnesia, MgO, is objectionable, as it causes the "slaking" process to be extremely slow, and may result in the damage of the goods by burning holes in them.

The method, and also the duration, of liming varies greatly in different yards, and also for different classes of goods in the same yard. Von Schroeder recommends the proportions of 6 lbs. of lime to 100 gals. of water. 6 per cent. of lime on the weight of the hides is known to be sufficient; many tanners, however, use 10-15 per cent. on the weight of the hides.

The two main systems of liming are the old French system and one in which the hides are taken right through the process in one pit. In the old French system the goods pass through three pits containing respectively an old, medium, and new lime. The new pit after having one pack of goods through becomes a "medium" lime, and the medium, in the same way, an old, while an old lime is run away after having the one pack of goods through. In the one-pit system the liquor is strengthened up from time to time by running away part and adding fresh milk of lime. The hides are simply laid horizontally one by one in the milk of lime and drawn out ("hauled") and replaced ("set") once, or even twice a day. Skins are frequently limed in paddles, and systems are in use in which the hides are suspended vertically in a pit in which the liquor is kept in movement by an agitator near the bottom of the pit. A method, used largely in America for sole leather, known as the Buffalo method, consists in treating the hides with lime for a short time, frequently with the addition of sulphides, followed by warm water, by means of which they are quickly in a condition for unhairing. Messrs Payne and Pullman* have patented a method by means of which lime is precipitated in the interior of the hide with a great saving of time and capability of modification according to the requirements of the goods. This is accomplished by treating the goods first in a 2 per cent. caustic soda solution, followed by a 1½ per cent. solution of calcium chloride. The previous treatment of the goods in a putrid soak liquor is necessary if the hair is to be removed, as the process does not accomplish this without the aid of bacterial action.

The time necessary for thorough liming varies with different classes of goods; hides are usually given from seven to ten days while sheep skins require a longer time.

The time of liming is greatly shortened by the addition of various substances which "sharpen" the lime. Sodium sulphide to the extent of ½-½ per cent. on the weight of the hides is a very common addition which loosens the hair very rapidly, and lessens the solution of hide substance. Alkaline carbonates accelerate the liming action by increasing the alkalinity of the solution. Red arsenic sulphide and calcium sulphydrate are also used. Sheep skins, from which the wool must be removed with as little damage as possible, are treated on the flesh side with a paste of lime and sodium sulphide, and laid in pile, and after a few hours the hair is pulled off without having come in contact with the alkali.

The hair is removed by working with a blunt knife (Fig. 229) over a sloping convex beam of wood with a zinc covering, and the hides are placed in water as soon as possible after that operation in order to prevent carbonation of the lime through contact with the air. It is often difficult to remove the short under hair which is more deeply rooted than the rest; this can often only be effected by shaving with a sharp knife.

There are several machines in use for the removal of hair; in the Leidgen machine, one of the most commonly in use, a cylinder fitted with blunt knives revolves against the surface of the hide which is kept in contact with it by the pressure of a rubber apron. The hides are also fleshed after the liming process. This is done with a heavy two-handled knife (Fig. 229) over a beam similar to the unhairing beam. The knife differs from the unhairing knife in having both its edges sharp, and the action is partly scraping and partly a cutting one; the mechanical action of the knife in forcing out fat, etc., is also important. Manual labour has, in this process also, been partly superseded by machines of which the Jones and the Vaughan fleshing machines are the most important.

Chemical Control of the Lime Yard.—The alkalinity of a lime liquor increases with its age owing to the formation of amines and ammonia as the final products of the splitting up amino acids

* English Patent, 2,873, 1898.

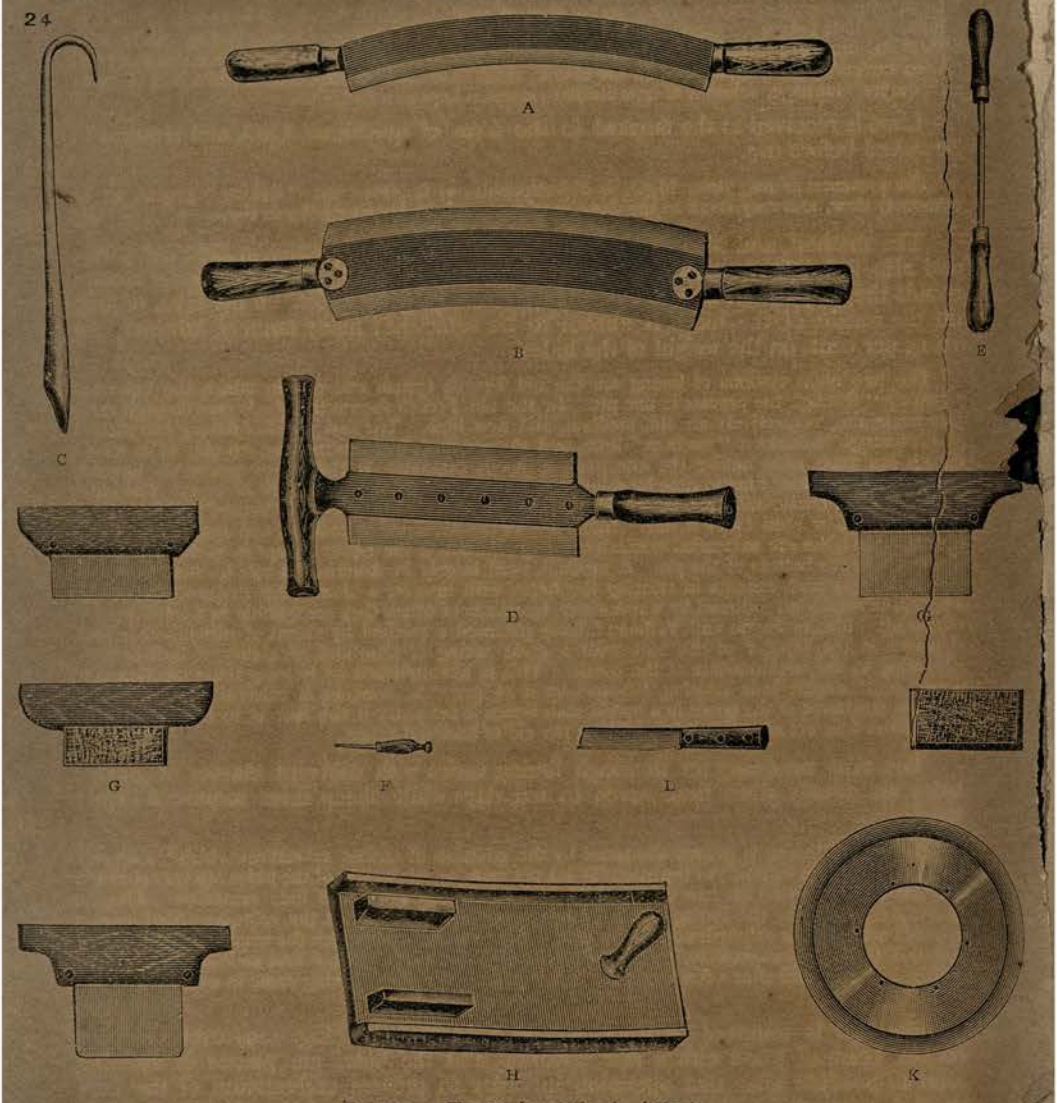

FIG. 229.—Tanners' and Curriers' Tools.

A. Unhairing Knife	D. Shaving Knife	H. Arm-Board
B. Fleshing Knife	E, F. Curriers' Steels	K. Moon Knife
C. Pit Hook	G, G. Slickers	L. Rounding Knife

derived from the hide substance. The alkalinity of a lime liquor in which lime alone has been used therefore affords a very good indication of its age. (A saturated solution of CaO at the ordinary temperature has an alkalinity of about 4.7 c.c. $\frac{N}{10}$ HCl per 10 c.c.)

Dissolved hide substance is determined by the usual Kjeldahl method after evaporating with a little dilute sulphuric acid. The percentage of nitrogen multiplied by 5.62 will represent the amount of dissolved hide substance.

A useful test of the amount of hide substance dissolved in a lime liquor has been proposed by Seymour-Jones. 50 c.c. of the filtered liquor is placed in a cylinder and made slightly acid; saturated salt solution is then added to make the volume up to 100 c.c. The greater part of the hide substance

is thus precipitated, and collects at the surface of the liquid, and by measuring its volume after a definite period of time the test may be made roughly quantitative.

Ammonia is determined by boiling the liquor for fifteen to twenty minutes in a flask connected with a condenser, and absorbing the ammonia evolved in a known volume of standard acid which is then titrated back. For improvements see Procter and M'Candlish.*

Sulphides may be estimated by the volumetric method, using zinc sulphate solution.

The Vegetable Tanning Materials

The present state of knowledge with regard to the constitution and classification of the tannins is unsatisfactory. In many cases each material contains a different variety of tannin, and the tannin even from the same plant may be of a different constitution as it resides in a different part of the plant (wood, bark, fruit, etc.). A certain broad distinction, however, may be drawn between the tannins according to their reaction with a solution of a ferric salt. Pyrogallol tannins yield a blue-black colour when treated in this manner, while catechol tannins give a greenish black colour. This distinction is, in the main, borne out in their behaviour when used as tanning materials. Catechol tannins also give a precipitate with bromine water which is not the case with pyrogallol tannins.

The constitution of two members of the pyrogallol group has been determined with reasonable certainty. These are gallotannic acid (from gall nuts), which is probably di-gallic acid, and yields gallic acid under the action of dilute acids and some unorganised ferments, and ellagitannic acid (usually present in mixture with gallotannic acid), which yields ellagic acid under the same conditions, and is the source of "bloom" deposited by some tanning materials, notably myrobalans, valonia, and divi-divi. The tannins of the catechol group, on the other hand, yield no gallic acid or bloom on boiling with dilute acids, but generally give a deposit of "reds," which are anhydrides of the tannin and insoluble in water. The lower anhydrides are not completely insoluble, and form the difficultly soluble portions of many tanning materials. They may be brought into solution completely by the use of alkalis or alkali sulphites, which is done to a great extent in the manufacture of soluble quebracho extracts. (See **Inks**, p. 490; and **Dyeing**, p. 548.)

Tannin is usually present to the greatest extent in the bark in the interior of thick-walled cells. The outer dead covering of bark ("ross") in most cases contains very little tannin. The percentage of tannin in wood is usually low, though in many cases its extraction is rendered commercially practicable by the cheapness of the raw material. Insect galls often contain a very high percentage of tannin which is here undoubtedly a morbid secretion of the plant induced by the puncture of the insect.

The following are some of the more important vegetable tanning materials:—

Algarobilla consists of the pods of several of the Cæsalpinias, chiefly *C. brevifolia*, a native of Chili. The tannin, being held loosely in the fibre, is very easily extracted. It is one of the strongest tanning materials known. A sample of the pods, freed from seeds, examined by the writer, showed 60.8 per cent. of tannin by the official method.

Babool, *Acacia arabica*.—The bark containing 12-20 per cent. tannin is used to a considerable extent in India. The pods, which also contain tannin, are used in India for bating.

Canaigre, *Rumex hymenosepalum*, is grown in Mexico and Texas. The tuberous roots contain when dried 25-30 per cent. of a catechol tannin. It is prepared by slicing thinly and drying rapidly, and gives a leather of a bright orange colour.

Chestnut, *Castanea vesca*.—The bark contains tannin up to 17 per cent. but is not much used as a tanning material. The wood, containing 3-6 per cent. tannin, is used in great quantity in the manufacture of chestnut extract.

Divi-divi, *Cæsalpinia coriaria*.—The tree is a native of Central America. The dried pods contain 40-45 per cent. tannin which is used as a partial substitute for gambier.

Gambier, *Nauclea gambir*.—A climbing shrub of the East Indies. The material appears in commerce as cube gambier, a hard earth-like substance containing about 45 per cent. tannin, and as block gambier containing 30-35 per cent. tannin and 35-40 per cent. water. Gambier is extracted from the leaves and twigs of the plant by chopping and boiling with water until the latter becomes

* *Journ. Soc. Chem. Ind.*, 1906, 254.

syrupy; the leaves are then removed. The liquid, on cooling, becomes a pasty mass which is cut into cubes and dried either by the heat of the sun or by wood fires.

Hemlock, *Abies canadensis*, hemlock fir.—The bark, containing 8-10 per cent. tannin, is used to an enormous extent in America and yields a dark red coloured leather. It is also the source of hemlock extract.

Larch, *Larix europea*.—The bark contains 10-12 per cent. tannin and is used to a great extent in the tannage of light leather, principally basils, to which it imparts a fine colour.

Oak.—The bark of many species of oak is used as a tanning material and was one of the earliest tanning agents used. The bark, containing about 10 per cent. tannin, is used to a great extent in the manufacture of sole leather, but has been replaced to some extent by extract made from the wood. Oakwood extract is also used for the tannage of sheepskins for roller leather.

Valonia, the acorn cups of *Quercus ægilops* from Asia Minor, contains about 35 per cent. tannin of which the larger quantity is in the "beard," and is much used in the manufacture of the heavier leathers.

Galls containing a large percentage of tannin are abnormal growths on various species of oaks produced by the puncture of insects, principally of the Cynips group. "Knoppern" are galls produced in the immature acorns of various species of oaks, principally *Q. Cerris*, and were formerly very largely used.

Myrobalans are the fruit of *Terminalia chebula*, a tree indigenous to India. They contain 30-40 per cent. tannin but vary a great deal in quality. They are divided into several grades known as "Bombays," "Jubbalpores," and "Vingorlas."

Quebracho, *Loxopteryngium Lorensii*.—The wood of the tree, grown principally in the Argentine, contains about 20 per cent. of a red difficultly soluble tannin. It is now used to an enormous extent in the form of extract, made, for the most part, in the quebracho forests. The greater part of the extracts are made completely soluble by the use of alkalis or sulphites.

Sumac, *Rhus coriaria*.—A shrub grown in great quantities in Sicily and Italy. The leaves and shoots are gathered, and after drying are finely ground, and as such the material appears usually in commerce. The ground sumac is "ventilated" or winnowed to remove sand and small particles of iron. It is divided into two grades, "mascolino," the best, which should contain 27-30 per cent. tannin, and "feminella" consisting of the inferior grades. Sumac is particularly liable to adulteration, principally with the leaves and stems of *Pistacia lentiscus*, the most important work on the detection of which was done by Andreasch.* Lamb and Harrison† have also published a very satisfactory method of detection of adulterants of sumac by microscopical means.

Wattle.—Many species of the genus *Acacia* are used as tanning materials in Australia, and may have a tannin content up to 50 per cent.

Synthetic Tanning Materials, or "**Syntans**," have been produced by E. Stiasny (see *Journ. Soc. Chem. Ind.*, 1913, **32**, 775) by heating phenols with formaldehyde in a slightly acid solution and then sulphonating the product to render it soluble. The Badische Co. put it on the market as "Neradol D." See also French Patents, 443,730, 1912; 451,875, 1912; 451,876, 1912; English Patents, 8,511, 1912; 8,512, 1912; 24,216, 1912; 24,982, 1912.

Extraction of Tanning Materials

The extent to which the preliminary grinding of the material is taken is of importance as it must be sufficient to allow as complete penetration of the water as possible, while avoiding reduction to a powder which would cake when wet, and result in clogging of the leaches. The most general method of extraction of tanning materials in use is the "press-leach" system. The leaches consist either of pits sunk in the earth constructed of brick and cement or wood, or vats or square receptacles above the surface of the ground. A set consists of any number up to twelve. Each is provided with a false bottom consisting of wooden laths on which the tanning material rests, leaving a space underneath to allow the removal of the liquor. All the leaches are connected by means of a pipe or "trunk" passing from the bottom of one into the top of the next right through the series. When in working order the leaches contain material in all stages of extraction, and the liquor from the strongest is run off for use in the pits. As strong liquor is drawn off from the head leach an equal quantity of water is pumped into the weakest, and floating on the top of the liquor in that leach forces some of it into the next, and so on through the whole series. By this means the nearly exhausted material is brought in contact with fresh water with consequent great thoroughness of extraction. Before the

* "Sicilianischer Sumac und seine Verfalschung," Wien, 1898.

† "Sumac and the Microscopic Detection of its Adulterants," *Journ. Soc. Dyers and Colourists*, March 1899.

material from the first leach is thrown out ("cast") it is finally extracted with hot water by which further quantities of tannin are extracted. The water is heated by blowing in steam or by an arrangement of steam coils below the false bottoms of the leaches, of which systems the latter, though costly, is preferable, as live steam is injurious to the leaches. A better system is that of using the silent-boiling jet, which is also used, as suggested by Professor Procter, to circulate the water in the vat, which results in very complete extraction of the material. The material in the first leach being exhausted, is "cast," and the leach refilled with fresh material. This leach then becomes the head leach of the system, and receives the liquor from what was previously the head leach. In the Holbrook system the liquor is pumped from one pit to another instead of being left to find its level under the action of gravity. Care is taken never to let a leach run dry, as the material would sink down and form a compact mass resulting in incomplete percolation through the formation of channels. Sprinkler leaches were formerly much used in America. The material was placed in round tubs fitted with a revolving pipe above for the delivery of the water. The water was sprayed upon the leach from small holes in the horizontal pipe as it revolved. The extraction with this system was very incomplete, and great loss of tannin was occasioned through oxidation.

Where the liquor is to be used in the manufacture of extract it is decolourised on coming from the leaches. It is mixed with a proportion of blood or albumen and heated to 70° C., at which temperature the albumen coagulates and carries down much of the colouring matter. Evaporation is carried out under reduced pressure in order to decrease loss of tannin by oxidation, which would occur if evaporated at atmospheric pressure. The Yaryan triple effect evaporator is greatly used for this purpose. By the use of this system, in which the steam from the weakest liquor is used to heat the second and so on, the liquor will pass through the whole apparatus in four or five minutes, and increase in density from about 1.02 to 1.20 without having been heated above 70° C.

The import of **tanning substances** into the United Kingdom in 1910 is shown in the following table:—

	1910.	Value.
Bark for tanning	560,000 cwt.	£226,000
Extracts for tanning	...	749,000
Gambier	5,000 tons	155,000
Myrobalans	861,000 cwt.	225,000
Sumac	11,000 tons	106,000
Valonia	18,000 cwt.	169,948
Various	21,000 cwt.	12,760

Sole-Leather Tanning

After the unhairing and fleshing process, hides for sole leather are "rounded." This is done with a sharp knife on a table, and enables the tanner to give a cheaper tannage to the inferior portions of the hide. In England the custom is to divide the hide into "butts" or "bends," which constitute the best part of the hide, and "offal," which includes the bellies, shoulders, and cheeks (Fig. 230). In America it is more usual to divide the hide, by a cut down the centre of the back, into "sides." Before the goods enter the tan liquors, some deliming process is necessary, as a brittle grain and bad colour would result if they were tanned in the condition in which they came out of the limes. Formerly, a simple washing in water was considered sufficient, supplemented by the acid in the earlier liquors, but now it is almost universally the custom to use an acid bath for this purpose. It is of great importance that the lime should not be completely removed as an excess of acid would be as injurious as that of alkali. The safest acid used is boric acid, and a great improvement in colour is effected by a treatment of the goods in a 1½-2

per cent. solution of this acid. Sulphurous acid is also good, and organic acids, such as lactic, acetic, and formic acids. Sulphuric acid yields good results, but great care is necessary to avoid excess.

The progress of the deliming action is easily followed by moistening the cut edge of the hide with an alcoholic solution of phenolphthalein when any free lime in the hide immediately produces a pink colour.

The object of the sole-leather tanner is to obtain weight, solidity, and waterproofness in his finished goods.

In earlier times this was accomplished by leaving the goods in comparatively weak liquors for a great length of time, the actual tanning process often taking from twelve to eighteen months, but the introduction of extracts and the consequent facility of producing much stronger liquors has, in most cases, shortened this time considerably.

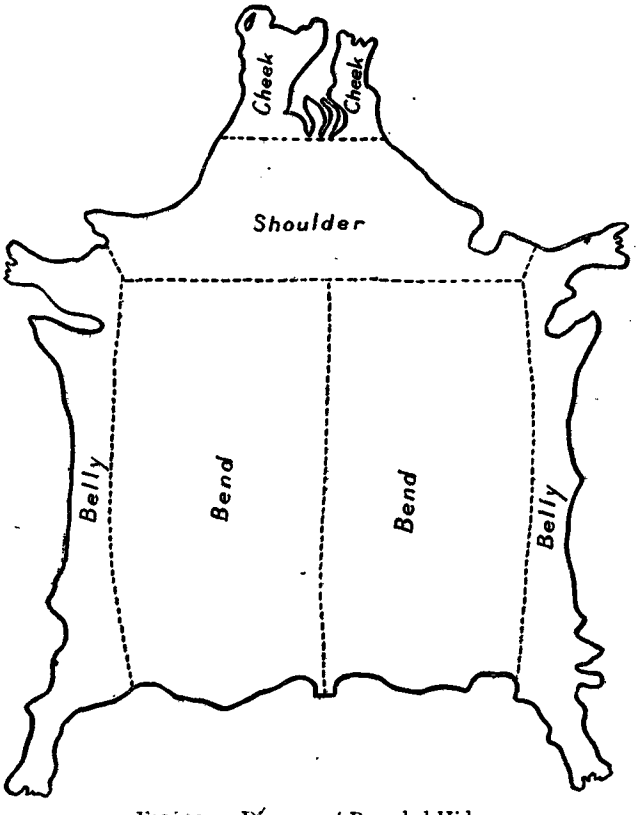

FIG. 230.—Diagram of Rounded Hide.

For even penetration of the tan a gradual increase in strength of each liquor into which the hide is removed is necessary, since diffusion will only take place from a region of higher concentration to that of a lower. The first pits into which the goods are placed are the "handlers"; the hides fastened on poles by one edge are hung vertically in the liquors and frequently moved, whereby the grain is fixed and an even colour is produced. The percentage of tannin in the handler liquors is low and the acidity relatively high $\left(\text{up to one-twentieth normal or even } \frac{N}{10}\right)$.

These conditions are usually attained by working the liquors "down the yard," *i.e.*, the pit from which a pack of goods has just been removed to go into the next stronger one of the series becomes the one below, and its place is taken by the one above it; thus the goods move in one direction and the liquors in the opposite. This system is also advantageous in that the astringent tannins have

already been removed by the goods, leaving only the milder tannins which are more suited to the green goods. The time occupied in the progress of the goods through the suspender varies from ten days to a fortnight; they then pass on to the "handlers." These are worked in systems of six, eight, or ten pits, and the goods are moved forward after being in each pit from six to eight days. The goods are in the handlers for a month to six weeks, and pass from a strength of liquor of about 20° Barkometer * to that of about 40° Bkr.

By the time the goods leave the handlers they will usually have become completely penetrated by the tan liquor, and the remainder of the tanning process has for its object the deposition of solidifying and weight-giving matter in the interfibrillar spaces. The final step in the tanning process is the laying away of the goods in the "layers" with ground tanning material dusted between each hide and the whole covered with strong tan liquor. By this means the hide is enabled to take up the more difficultly soluble tannins, and a solid and dense leather is the result. The goods are drawn several times and laid down again with fresh quantities of tanning material and stronger liquors, which may reach a strength of 120°-150° Bkr. where extract is used. The time in layers may extend from three to six months.

Of the materials used in the tannage of sole leather, oak bark is one of the oldest and gives a result which is said to be superior to that obtained by any other material, but its low percentage of tannin and the lightness in weight of the finished leather tanned in this way have caused its replacement in many cases by extract. Valonia is used to a great extent, as it gives heavy and solid leather and deposits much bloom. Gambier is used to some extent, the mildness of its tannin making it especially suitable for the strengthening of the suspender liquors. Oak wood, chestnut wood, and hemlock bark extracts are very largely used, principally for strengthening the layer liquors.

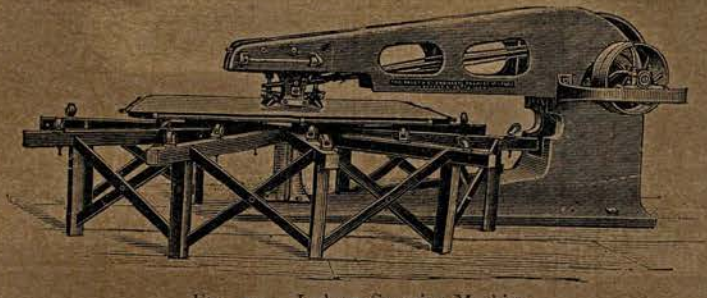

FIG. 231.—Jackson Scouring Machine.

The process of **tanning dressing leather** is similar to that for sole leather, with the difference that as resulting leather is required to be soft and flexible the process is modified accordingly. A lighter class of hides are used, such as kips, or the goods are reduced in substance by shaving. The main point of difference in the method is the introduction of the "bating" process. This consists in submitting the goods to the action of a fermented infusion of hen or pigeon dung. The proportions used are variable, ranging from 12-60 l. per 1,000 kilos. raw hide in 2,000 l. of water. By this means a great portion of the lime is removed and a considerable solution of hide substance occurs. The mechanism of the action of the "bate" is probably analogous to that of the puer (see p. 580). The hides after becoming soft and fallen are usually "scudded" over the beam, in which process much dirt and grease are worked out, and then frequently given a further treatment in an acid bath to remove the last traces of lime before entering the tan liquors.

The tanning is usually commenced, in this country, in paddles, but suspenders are used where a very smooth grain is desired. As bloom is not required in this tannage the use of bloom-giving tanning materials is avoided.

Sole leather after leaving the layers is washed through a clean liquor or warm water, and "scoured" with stone and brush by hand or by machine (Fig. 231) till

* The Barkometer is a form of hydrometer, and is of great service in controlling the strength of liquors of which the composition is the same. As it shows all solid matter in solution, however, the strength of a liquor in tannin, as shown by it, can only be relatively correct.

all bloom is removed from the grain surface, half dried ("sammed") and laid in pile to temper. A treatment in a strong liquor made from sulphited quebracho extract is frequently given, which results in a better colour in the finished leather though producing considerable loss of weight by the action of the sulphite on the

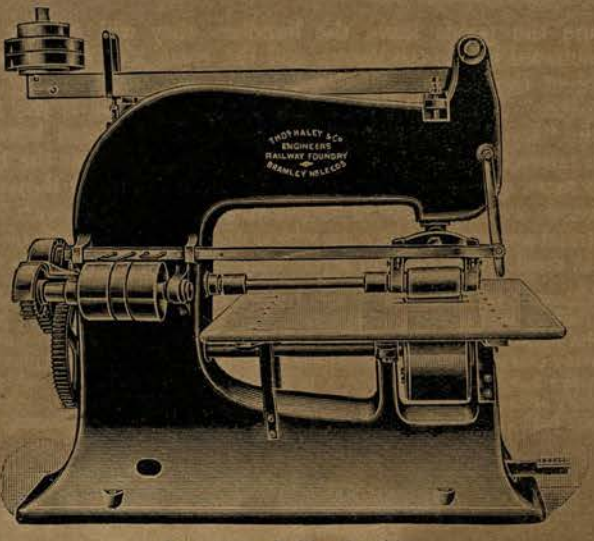

FIG. 232.—Rolling Machine.

tannin held in the leather. It is then "struck out" either with the "pin" or by machine which smooths and flattens the grain. The goods are then rolled by machine, once with a light roller when the grain is somewhat moist, and finally, when nearly dry, with the heavy roller (*Fig. 232*). They are then dried by the aid of moderate heat, and after polishing with a brush are ready for sale.

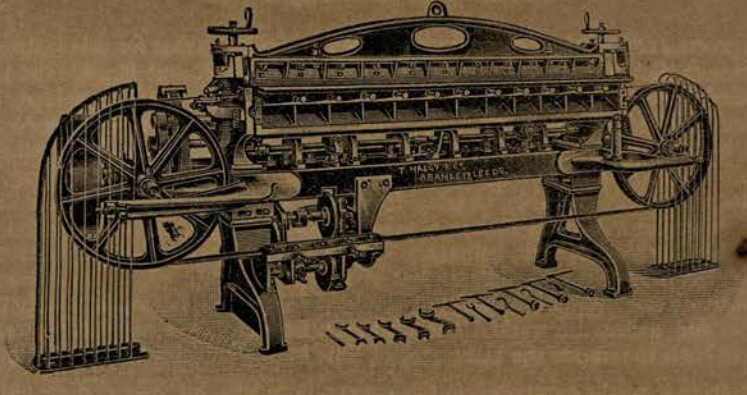

FIG. 233.—Band-Knife Splitting Machine.

A light coating of oil is frequently applied to the grain side before drying in order to cause the evaporation to take place through the flesh side, as otherwise the uncombined tannin would be deposited on the grain and, oxidising, cause the latter to be brittle and of a bad colour.

The **finishing of dressing leather** (for strap butts, harness, belting leather, etc.) differs essentially from that of sole leather in the inclusion of the "**stuffing**"

process; this consists in impregnating the leather with a mixture of solid and liquid fats and greases, rendering it supple and impervious to water. The leather is scoured with stone, brush, and sleeker to remove bloom, and reduced in thickness. This is done by shaving by hand or machine, or by splitting the goods.

Shaving by hand requires great skill and is done over a nearly vertical beam with a two-handled knife (Fig. 229) with an edge turned at right angles to the surface of the blade. Of splitting machines for this purpose the band-knife machine (Fig. 233) is the most important; with this machine the leather is held and moved forward by rollers against the edge of an endless ribbon-knife, passing round a wheel at either end of the machine.

The leather must be in a moist state before stuffing, and the exact degree of dampness is a matter of some importance. It should generally be such that water exudes from the pores when the leather is pinched.

The two methods of stuffing most commonly in use are hand stuffing and drum stuffing. In hand stuffing the leather is coated on the flesh side or on both sides with a mixture of fats known as "dubbing," consisting usually of cod oil and tallow. The mixture is melted together and stirred as it cools in order to obtain a homogeneous pasty mass, and the proportions of hard and soft constituents are modified according to the season and the temperature at which the leather is to be dried. Much of the solid crystalline fats remain on the surface of the leather after the remainder has penetrated to the interior, and are scraped off with the sleeker and used again. The temperature at which the stuffed leather is dried is adjusted so that the dubbing is kept in a soft condition, but not so high as to render it liquid.

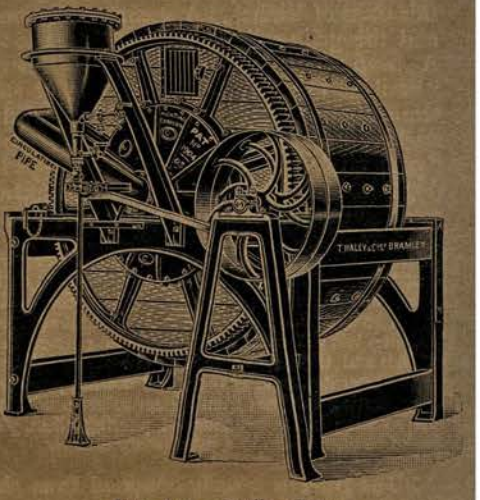

FIG. 234.—Stuffing-Drum.

In "drum stuffing" the goods are treated in a revolving drum (Fig. 234) with the stuffing mixture. The drum, previous to putting in the goods, is heated by blowing in hot air or steam, or frequently a steam coil is fixed in the drum itself. The temperature of the interior of the drum may be safely raised to 60° C. if cold, damp leather is introduced. After the goods have been drummed sufficiently long to have reached the temperature of the interior the stuffing grease is introduced either through the door or run in through a hollow axle. A very large quantity of grease can be taken up by leather without detriment to its light colour which reappears on bending sharply in "boarding." Advantage is frequently taken of the facility with which adulterants can be introduced into the leather in drum stuffing; glucose and barium sulphate are the most common of these, and produce a fictitious weight together with an improved colour to that obtained by an equivalent quantity of grease.

A method of dry stuffing practised in Germany is termed "Einbrennen." Melted tallow is poured over the leather, which must previously have been completely dried, and allowed to sink in by holding over a fire. Another method is to dip the leather completely into molten tallow.

Stuffed leathers are particularly liable to a defect known as "spueing," which is of two kinds. The first, which is by far the least objectionable, is due to the crystallisation of the hard fats on the surface of the leather, and causes no injury to the leather. The other kind is due to a chemical change taking place in the stuffing materials, and makes its appearance as resinous spots or pimples on the surface of the leather. It is usually attributed to adulterated oils, but occasionally appears when the purest cod oil has been used. As it is caused by oxidation of the oil, it is liable to appear when conditions are such as to favour this action, such as moist heat with little ventilation and the catalytic action of iron salts used in the production of black goods.

Fats and oils are also introduced into the leather by "fat liquoring." In the preparation of a fat liquor the oil is reduced to an extremely fine state of division by the use of suitable emulsifying agents. By drumming the goods with such a mixture they may be made to take up a large quantity of oil without acquiring a greasy feel.

Light Leather

The raw material for the manufacture of light leather may be taken as consisting of the skins of sheep, goats, and calves. The method of treatment up to the end of the liming process is practically the same as that for heavy leather except that the liming of sheep and goat skins is usually of a somewhat longer duration, as a soft and supple character in the finished article is required. Sheep skins are usually received at the tan-yard from the fellmonger after the wool has been removed, so the only object of the liming process is to plump the skin and render it in a suitable condition to take up the tannin from the liquors. The main difference between the tanning processes of light and heavy leather is in the condition in which the goods enter the tan liquors. By the treatment subsequent to liming the skins are almost entirely deprived of lime and brought into a soft and flaccid condition, which is essential in order that the finished product may possess the qualities required in this class of leather. A great proportion of sheep skins are split when fully limed and the grain split tanned into "sumac skivers," while the flesh split is oil tanned. A sheep skin tanned by a vegetable process without splitting is termed a "roan" or "basil." The goods, after fleshing or splitting, are washed in paddles in order to remove some of the lime. A little acid is frequently added to the water in the washing paddle in order further to promote this action. The goods are then "**puered**," which operation consists in paddling in a weak warm infusion of fermented dog-dung. By this means a further quantity of lime is removed, and considerable solution of skin substance and emulsification of fats takes place.

The mechanism of the puering process has been investigated by J. T. Wood, who has shown that the effect on the skins is due to the joint action of amines and their compounds, and enzymes produced by the metabolism of bacteria which exist in the puer liquor in great quantity. Wood has found that a puer liquor which has previously been boiled and so freed from living organisms and enzymes has still considerable action on limed skin owing to the removal of lime by the action of amines and their compounds. The liquor treated in this way, however, had no dissolving action in the interfibrillar substance, and did not produce the characteristic properties of puered skin. By precipitating enzymes from a puer solution with alcohol and redissolving in water it was found that the solution had a pronounced puering effect. A mixture of the two classes of active bodies was found to puer a skin in a satisfactory manner.

The **puer** is usually obtained from the kennels and, coming from this source, contains less lime than usual; it is allowed to ferment for some weeks before use, by which its activity in the direction required is much increased.

A perfectly satisfactory substitute for dog-dung for puering all classes of goods has yet to be discovered. The earliest scientific attempt at providing a substitute was made by Wood, Popp, and Becker with "**Erodin**," by the use of which perfectly satisfactory results may be obtained with some classes of goods. Erodin consists of a solid nutrient medium together with a pure culture of bacteria which have been found to be especially active in the puering process. The nutrient medium is dissolved and suspended in water which is raised to a temperature of 104° F., and the pure culture of *Bacillus erodiens* added. The bacteria are allowed to grow in the medium for about three days, and the temperature is raised to 104° F. every night and morning during that period by admitting steam to the culture. The liquid is then diluted and used in the same manner as a natural puer liquor.

Of the later puer and bate substitutes brought on the market, "**Oropon**," manufactured by Röhm & Haas, Darmstadt, is being used to a great extent. This consists of a mixture of ammonium chloride and pancreatic enzymes held in fine sawdust as inert material.

The operation of puering is one requiring great experience and care to obtain the best results. If the temperature is allowed to become too high, or the skins left in puer liquor too long, the goods may be badly damaged or even completely destroyed by excessive bacterial action. Frequent change of position is necessary

in order that the action may be regular, so the goods are usually kept in motion during the whole operation by means of the paddle. The skins are removed from the paddle when sufficiently "fallen," a point to determine which requires a practised touch and great experience. The goods are then "scudded" on the flesh side with a blunt knife by which treatment much grease and dirt are worked out; the operation is sometimes carried out by machine.

The skins are then "**drenched**," which consists in submitting them to the action of a fermenting infusion of bran, and removes a still further quantity of lime and causes slight plumping.

J. T. Wood and Willcox* have also studied the action of the bran drench upon skins, and have found that the acids produced in the bran fermentation are the active agents in removing lime and plumping the goods. Wood gives the following typical analysis of the acids found in a working drench:—

Formic acid	0.0306 g. per litre.
Acetic acid	0.2402 ,, ,,
Butyric acid	0.0134 ,, ,,
Lactic acid	0.7907 ,, ,,

The most important living organisms found in the drench were two species of bacteria named by their discoverer *Bacterium furfuris* α and β. The two were very similar in character, but produced a slightly better fermentation together than when used separately. The same liability to damage of the skins is present in the drenches as in the puer liquors, particularly through a butyric fermentation which may take place in hot weather, resulting in rapid swelling and solution of the skins.

The quantity of bran used in the drenching process is variable, but an average of about 5·10 per cent. on the weight of the skins is usually taken and infused in water in the proportion of about 4 parts of bran to 1,000 of water. The mashing is carried out at a temperature of about 90° F. and fermentation started by adding a few pailfuls of a working drench. The goods are then added and as the fermentation proceeds are brought to the surface by the gas which is evolved in great quantity during the fermentation.

Thin skins may be drenched sufficiently after the first "rising," but heavier goods are put down several times before sufficiently acted upon. Experience is necessary in judging the point at which a skin is sufficiently drenched, the feel of the goods affording the best criterion. The skins become white and soft, and retain the impression made when pressed with the finger.

The use of the bran drench has been to some extent replaced by that of acids, of which lactic acid is the most commonly used. The goods are paddled in a solution of about 2 lbs. of the acid in 100 gals. of water at a temperature of 30°-35° C. The process is quicker and safer than that of using bran, but the effect produced on the goods is not exactly the same.

The "C.T. Bate" manufactured by the Martin Dennis Chrome Company is also used for removing lime, and is suitable for use as a substitute for drenching. It consists mainly of the sulphonic acids of naphthalene and probably other hydrocarbons, and its antiseptic character may also render it useful in arresting putrefaction.

Gallic acid is capable of bating and its use as such has been patented. It is probably the active agent in the fermented infusion of babool pods, which is much used in India for deliming.

Tannage of Light Leather

The materials used in the vegetable tanning of light leather are very various. Previous to entering the tanning pits the goods are usually treated in the paddle with a very weak solution of the tanning material, where they remain until coloured through. The movement obtained by paddling is essential in causing even absorption of the tannin and producing a fine grain. In some cases the entire operation of tanning is carried out in the paddle, notably in the tanning of sumac skivers.

After colouring through the goods are passed through a series of pits in a manner similar to that of heavy leather tanning. The strength of the liquors, however, is

* *Journ. Soc. Chem. Ind.*, 1890, 27; 1893, 422; 1897, 510. "Brit. Ass. Rep.," 1893, 723.

much less as is also the acidity of the earlier liquors, as no solution of lime is necessary, it having been almost completely removed in the earlier treatment as described above. Materials which yield "bloom" and a solid character to the leather are avoided, as the main results aimed at in the manufacture of light leather are suppleness and the best possible appearance of the grain. A great proportion of sheep skins are tanned into sumac skivers after splitting when fully limed.

A common process to which the goods are submitted previous to entering the sumac liquors is that of "pickling." After leaving the drenches the grains are paddled in solution of common salt and acid. The usual acid employed is sulphuric acid, on account of its cheapness, but the use of organic acids such as acetic and formic acids has lately been recommended, and has some advantages. A drawback to the use of sulphuric acid is the tendency which traces of it left in the leather have to cause rottenness after the lapse of time.*

After the uniform penetration of the acid and salt the goods are placed for a short time in a saturated solution of salt. The pickling process permits the skins to be kept for any reasonable length of time in an unchanged condition, and is resorted to when goods are to be exported in the untanned condition. The liquors in which pickled goods are tanned must contain a certain quantity of salt as fresh water produces a strong swelling action on the goods.

The skins are then placed in the paddle (Fig. 235) with water and ground sumac, and kept in

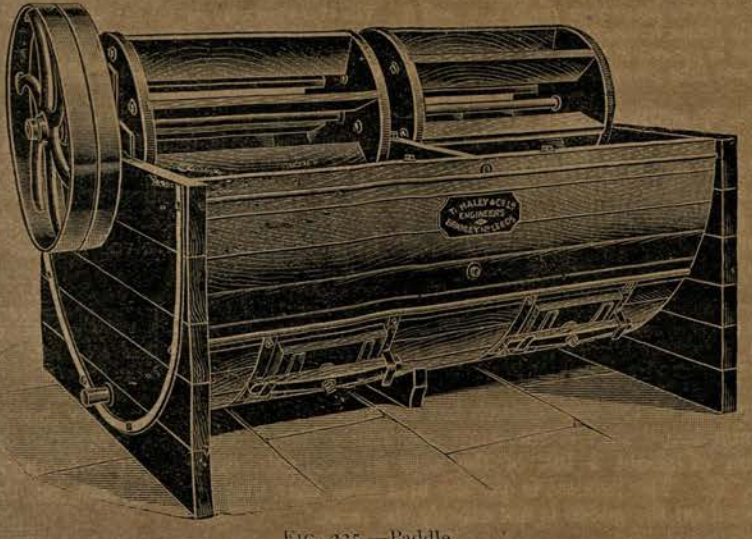

FIG. 235.—Paddle.

circulation until the tanning is complete. The light character of the skins and the movement of the paddle combine to render the tanning operation very short.

A method of tanning with sumac sometimes used consists in sewing each two skins together in the form of a bag, with the grain on the outside. The interior is filled, through a small hole, with strong sumac infusion and some powdered sumac, and after closing the aperture the skins are floated on a warm sumac liquor. After leaving in the liquor for a short time the skins are placed in a pile, and the sumac infusion is forced through the pores of the skins by their own weight. The process is repeated once or twice, which results in the skins being fully tanned in a very short time. A similar method is employed in the manufacture of morocco leather from goat skins.

As stated above, the method of tannage of basils and calf skins with bark and vegetable extracts resembles that of sole leather except that weaker liquors are used throughout the series of pits, and that the goods are not usually laid away with the solid material to complete the process.

Dyeing

The skins of sheep naturally contain a large quantity of animal grease which must be removed before a level dyeing can be obtained. This is done either by hydraulic pressing before tanning

* *Soc. of Arts Journ.*, 1901, 14.

or by the use of a solvent after the tanning process. The dyeing of vegetable-tanned leather is performed either in the tray or in the drum or paddle. In the former method the skins are usually dyed in pairs, each pair being pressed firmly together, flesh side in, which results in the flesh side remaining undyed. This results in a saving of dye and a white flesh side which is desirable in some classes of goods. Dark coloured or stained leather is improved before dyeing by treatment with a 1-2 per cent. sulphuric acid solution or preferably with an organic acid.

The use of aniline colours has for the most part replaced that of the natural colouring materials, except in the production of blacks for which logwood is still used to some extent.

Either acid or basic colours are used; in the latter case a mordant such as tartar emetic is used. Titanium potassium oxalate has lately come into use to a great extent, the yellow colour which it produces in combination with tannin rendering it of great use when similar shades of colour are to be applied to the leather. When acid dyes are used, it is customary to add a small quantity of acid to the dye bath for the purpose of liberating the colour acid.

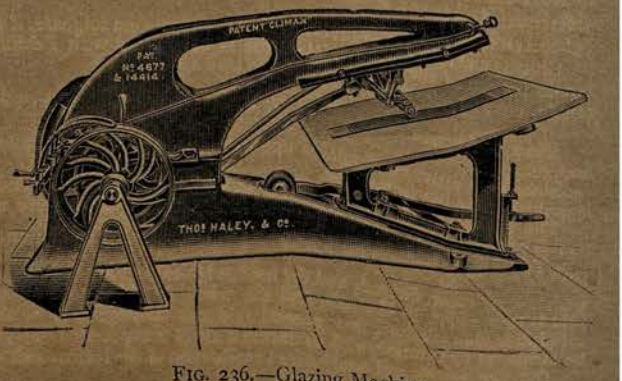

FIG. 236.—Glazing Machine.

Another method of dyeing which is used to some extent for light leather and almost universally for the heavier leathers is that of staining. In this method the colour is applied to the slightly damped surface of the leather by means of a brush, several coats being given if necessary with partial drying between each application.

After dyeing the grain surface of the leather is rendered glossy and smooth by the application of a "finish" of a mucilaginous nature, or by the use of a seasoning preparation followed by glazing by machine (Fig. 236).

Chemical Control of the Tanyard

The quantitative analysis of the vegetable tanning materials presents many difficulties, and it is only by strict adherence to standardised methods of analysis that different workers can obtain concordant results. The International Association of Leather Trades' Chemists have formulated rules for the sampling and analysis of tanning materials, and reference should be made to these for details of the process.

The Löwenthal Method of tannin analysis requires the following solutions:—

1. Potassium permanganate, 0.5 g. per litre.
2. Sodium sulphindigotate, 5 g., and strong sulphuric acid, 50 g. per litre.
3. Pure tannin, 3 g. per litre, for determining the tannin value of the permanganate.

25 c.c. of the indigo solution is placed in a beaker and diluted with ¾ l. of tap water. The permanganate solution is then run in from a burette until the colour becomes a pure yellow.

5 c.c. of the tan liquor is then taken in addition to the indigo and the titration repeated.

The difference between the two titrations represents the total oxidisable matter present in the liquor. The liquor is then detannised in the following way: 25 c.c. of 2 per cent. gelatine solution, and 25 c.c. of saturated salt solution containing 50 c.c. concentrated sulphuric acid per litre are added to 50 c.c. of the liquor and shaken for five minutes and filtered with the addition of kaolin if necessary. The filtrate is titrated in the same manner with the permanganate, twice the volume being taken to allow for the dilution. Detannisation is more conveniently done by shaking with hide powder, as in the official method, or with chrome shavings if available. The amount of permanganate equivalent to the tannin in the solution is thus equal to the difference of the titrations before and after detannisation. By determining the permanganate value of the standard solution of pure tannin the strength in tannin of the liquor may be easily calculated.

Acidity of tan liquors is determined by Procter's method by adding saturated lime water from a burette to 10 c.c. of the perfectly clear liquor in a beaker till the first trace of permanent turbidity appears.

The Analysis of Leather

The complete analysis of a sample of vegetable tanned leather consists in the determination of: (1) Water; (2) fatty matter; (3) water soluble matter, including—(*a*) uncombined tannins, (*b*) non-tannins; (4) insoluble matter, including—(*a*) hide substance, (*b*) tannin.

Water is determined by drying finely divided leather at 100° C.

Fats are determined by extracting with petrol ether in a Soxhlet apparatus.

Water soluble matter is estimated by digesting the extracted residue from the fat determination for some hours with 200 c.c. of distilled water at 15°-20° C., and then extracting in a similar method to that employed for tanning materials. The temperature of the water used for extraction is kept low to avoid decomposition of the leather. The proportions of tannin and non-tannins in the extract are differentiated as in the analysis of tannin materials by determination of total solids in the solution before and after detannisation.

Glucose and mineral adulterants, such as magnesium sulphate, if present, will be found in the non-tannin portion of the extract. Glucose is determined with Fehling's solution after removal of the tannin, etc., by precipitation with basic lead acetate.

Hide substance is estimated by determining the nitrogen (Kjeldahl method) in the original sample.

Since hide substance contains approximately 17.8 per cent. nitrogen, the percentage of nitrogen is multiplied by the factor 5.62.

The estimation of **free mineral acid** is very important, and is best carried out by Procter and Searle's method. 2 or 3 g. of the finely divided sample are moistened in a platinum crucible with 25 c.c. of $\frac{N}{10}$ sodium carbonate solution, evaporated to dryness, thoroughly carbonised, extracted with boiling water, filtered, and the residue ignited in the crucible. 25 c.c. of decinormal hydrochloric acid is then added to the ash, and the whole is added to the filtrate previously obtained. If the solution is then alkaline, free mineral acid may be assumed to be absent, but if acid the amount may be measured by titration with decinormal alkali using methyl orange as indicator.

The quantitative and qualitative examination of the leather **ash** will often afford valuable information with regard to the tannage, etc.

Mineral Tannages

Of the mineral tanning processes, the most important is that involving the use of the salts of **chromium**. Though of only very recent origin the process has already become a very serious rival to the vegetable tannages, and even, in some cases, has replaced them to a great extent.

There are two general methods of tanning with chromium compounds known respectively as the "one-bath" and the "two-bath" processes. In both methods the actual tanning agent is the same, the fibres being isolated and rendered imputrescible by the deposition on them of a basic chrome salt. In the one-bath process this is accomplished by immersing the skin in a basic solution of chromium sulphate or chloride, while the two-bath process consists in saturating the skin in a solution of chromic acid, and then submitting it to the action of a reducing bath whereby the actual tanning agent is formed in the interior of the skin. Professor Knapp in 1858 was the first to devise a practicable chrome tanning process which consisted in treating skins with a basic chromium chloride solution made by adding sodium carbonate to a solution of normal chromium chloride. The process was revived and patented later by Martin Dennis,* who put on the market a basic chrome tanning liquor prepared by dissolving chromium hydrate in hydrochloric acid, and rendering sufficiently basic with sodium carbonate.

The earliest two-bath process was proposed by Augustus Schultz in 1884. The method as patented by him consisted in paddling or drumming skins in a solution of 5 per cent. bichromate of potash and 2½ per cent. hydrochloric acid or an equivalent amount of sulphuric acid, till evenly coloured through with the chromic acid. The second bath consisted of a solution of sulphurous acid or an acidified solution of sodium thiosulphate.

The one-bath process is, of the two, the more analogous to the vegetable tanning process. Eitner † has shown that the basicity to which the chromium salt is brought is of extreme importance. A solution of a normal chromium salt penetrates the skin with great rapidity, but is very easily washed out, and a thin and lightly tanned leather results. As the salt is rendered more basic the rapidity of

* U.S.A. Patent, 495,028, 1893; 511,411, 1893; 7,732, 1893.

† *Gerber*, 1901, 3.

its penetration into the skin is less, but its absorption is more thorough, and the chrome is fixed more strongly. If the basicity, however, is rendered excessive, part of the chromium is precipitated as hydrate, and an insufficiently basic salt is left, resulting in very slow penetration of the tanning agent and overtanning at the surface of the skin, whereby the grain is rendered tender and even brittle.

Eitner considers as the most suitable the salt $CrOH.SO_4$, which is produced by the addition of 106 parts by weight (1 molecule) of dry sodium carbonate to 998 parts (1 molecule) of chrome alum.

Procter* has published a method of preparation of a one-bath solution by the direct reduction of bichromate with sugar in the presence of such a limited amount of hydrochloric or sulphuric acid as to result in a chromium salt of the required basicity. Suitable proportions are 5 molecules of HCl to 1 molecule of potassium dichromate, which results in the formation of a salt of approximately the formula of $Cr_2Cl_3(OH)_3$.

A stock one-bath chrome liquor may be made by dissolving 10 parts of chrome alum in 80 parts of warm water and adding, with constant stirring, a solution of $2\frac{1}{2}$-$3\frac{1}{2}$ parts of washing soda dissolved in 10 parts of water.†

Stock liquors which are bought ready made up and only requiring dilution with water are used to a great extent.

The product of the **two-bath process** differs from that of the one-bath in containing free sulphur, which is deposited in the leather from the decomposition of the thiosulphate used in the reduction.

In the first bath the following reaction takes place:—

$$K_2Cr_2O_7 + 2HCl = 2KCl + 2CrO_3 + H_2O,$$

the free chromic acid being absorbed by the skin. Heal and Procter‡ have shown that pelt absorbs no free chromic acid from a solution of potassium dichromate unless free chromic acid has previously been formed by the addition of acid.

The reactions taking place in the second bath have been studied very carefully by Eitner,§ who has shown that the following reactions take place when acid is added gradually to the thiosulphate solution.

On the addition of a small quantity of acid the skins become brownish from the formation of chromium dioxide or basic chromic chromate, $Cr_2CrO_4(OH)_4$.

(1) $$3CrO_3 + 6HCl + 6Na_2S_2O_3 = 3Na_2S_4O_6 + 6NaCl + 3H_2O + Cr_2O_3.$$

On adding more acid the colour of the skins becomes brighter from the formation of chromium chloride.

(2) $$2CrO_3 + 12HCl + 6Na_2S_2O_3 = 3Na_2S_4O_6 + 2CrCl_3 + 6NaCl + 6H_2O.$$

Further addition of acid results in the deposition of sulphur, partly in the skins and partly precipitated in the bath.

(3) $$2CrO_3 + 6HCl + 3Na_2S_2O_3 = 3Na_2SO_4 + 3S + 2CrCl_3 + 3H_2O.$$

After all the acid has been used up, further reactions take place between the chromium salts and the excess of thiosulphate, resulting in the formation of basic chromium salts and of more free sulphur.

(4) $$Cr_2(SO_4)_3 + Na_2S_2O_3 + H_2O = 2CrOH.SO_4 + SO_2 + S + Na_2SO_4.$$

(5) $$2CrCl_3 + Na_2S_2O_3 + H_2O = 2CrOH.Cl_2 + SO_2 + S + 2NaCl.$$

As the acid is, in practice, added in small quantities at a time the reactions will take place, in the main, according to these equations, but will always to some extent proceed simultaneously.

The proportions of dichromate and acid in the first bath, as used in practice, are very variable, the more important constituent being the acid, as it is only the free chromic acid which is thereby liberated which is absorbed by the skins. In Eitner's first bath sufficient acid is added to liberate the whole of the chromic acid, but a less quantity than this is frequently used. Absorption of the chromic acid by the skins is very rapid, and by drumming in the solution the skins are soon caused to take up the maximum amount. After leaving the first bath the goods

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* *Leather Trades' Review*, 12th January 1897.
† *Ibid.*
‡ *Journ. Soc. Chem. Ind.*, 1895, 251.
§ *Gerber*, 1900, 297.

are piled on a "horse" and allowed to remain so for some hours or overnight, whereby better fixation of the chrome is obtained. When in this state the goods are carefully protected from the action of light, which results in the reduction of the chrome at the expense of the skin and thereby causes irregular tanning.

Before entering the second bath the skins are frequently drawn through a strong "hypo" bath in order to fix the chrome on the surface of the skin which prevents "bleeding," *i.e.*, diffusion of the chromic acid solution into the hypo bath. The most usual reducing agent is a solution of sodium thiosulphate ("hypo") rendered acid with hydrochloric acid, and in this bath also great variations in the proportions used are met with in practice. It is usual to add the acid in small quantities at a time as the reduction proceeds, as the reduction is rendered more even and there is less loss by escape of sulphur dioxide into the air. Eitner suggests 12 parts of hypo dissolved in 400 parts of water, and 6 parts of 40 per cent. hydrochloric acid per 100 parts of wet pelt, less acid, however, being required if equal parts of acid and dichromate have been used in the first bath.

The operation of neutralising follows that of tanning, and is carried out in the same manner for leather tanned by either of the processes. When a two-bath process has been used the skins contain a considerable quantity of free acid which must be removed; and with one-bath leather the neutralising process results in further fixation of the chrome in the leather fibre. The skins are drummed in a dilute solution of a weak alkali of which several are in use, such as sodium bicarbonate or dilute ammonia. Borax is used to a great extent, its weakly alkaline nature rendering it the safest neutralising agent, and lessening the danger of over-neutralisation. The neutralising process is considered to be complete when a piece of blue litmus paper is not turned red on application to the freshly cut surface of the skin. Over-neutralisation to the extent of rendering the interior of the skin distinctly alkaline is carefully avoided, as the presence of free alkali in the skin is as objectionable in its effects as that of free acid. Eitner has recommended the use of silicate of soda as a neutralising material, and sodium hyposulphite and whitening have also been used. After neutralisation the goods are thoroughly washed in the drum in a stream of running water.

A peculiarity of the chrome process is that the goods are usually dyed and fat-liquored immediately after tanning, as if they are once allowed to become thoroughly dry it is impossible for them to be "wetted down" again sufficiently for even dyeing.

Fat liquoring, which is done either before or after the dyeing process, consists in drumming the skins in an emulsion of soap and oil which is absorbed very readily, and gives a plump and soft feel to the leather which would otherwise, from the nature of the tannage, be harsh and empty.

Many different formulæ for the preparation of fat liquors are in use, and various oils, such as castor, olive, cod, and neat's foot, are suitable. Sulphonated or turkey-red oils have lately been used to a great extent, and being soluble in water need no addition of soap as an emulsifying agent.

By drumming with a solution of glycerol or sugar chrome leather may be dried sufficiently to allow of the operations of shaving or staking before dyeing, the hygroscopic nature of these bodies rendering it possible to wet down the leather subsequently sufficiently for dyeing.

Chrome leather may be dyed direct with many of the acid aniline colours, but where basic colours are to be used the goods are given a tannin mordant by drumming or paddling with sumac infusion or gambier.

After dyeing the goods are thoroughly dried by hanging in heated stoves, and then, if necessary, the natural animal grease is removed by extraction with a solvent in a plant specially devised for that purpose. They are then brought to the necessary degree of dampness for the subsequent treatment by laying away among damp sawdust. Being now stiff and hard they are softened by staking, which is done by a machine which draws a blunt-edged blade along the flesh side of the skin, which is held against it by rollers (Fig. 237). The appearance of the grain is then improved by the application of a "finish," which usually contains blood or albumen, followed by "glazing" by friction of a glass or agate "stone" under pressure. This operation

is frequently repeated several times, and ironing with a hot iron completes the process.

Of the lighter leathers tanned by the chrome process calf skins, which are manufactured into "**box-calf**" or "**willow-calf**" (usually by the one-bath method), form a large proportion. In the manufacture of these goods, the operation of "boarding" (Fig. 229) (whereby the grain of the leather is raised) is included in the finishing process.

The manufacture of **glacé kid** from goat skins has attained gigantic proportions. Sheep skins are also chrome tanned to imitate real glacé kid.

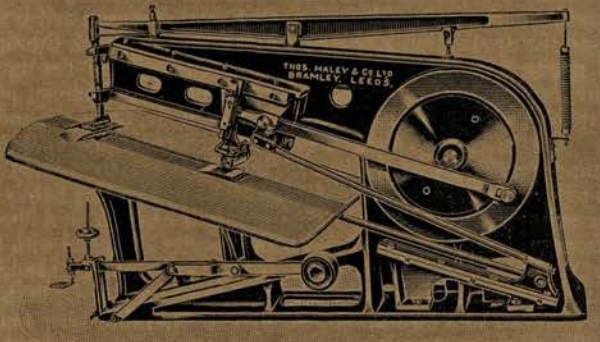

FIG. 237.—Staking Machine.

The production of chrome sole leather has not yet been brought to a satisfactory state, the leather having a tendency to become slippery under the influence of water; for belting and hydraulic leathers, however, the process is greatly used.

The chrome process is frequently combined with one of the vegetable tanning processes, the product being known as "**semichrome.**" The order in which the two tannages are applied varies, but a one-bath chrome tannage is necessarily used. The method is more particularly applied to the imported native-tanned sheep or goat skins from India (Persians). Before chroming, as much as possible of the vegetable tanning material is removed by drumming the leather in a dilute alkaline solution ("stripping").

Chemical Control of the Chrome Process

One-Bath Liquors.—The chromium in one-bath chrome liquors may be estimated gravimetrically by precipitation as Cr_2O_3 with ammonia, but more quickly and conveniently volumetrically. The chromium is converted into sodium chromate by treatment with sodium peroxide and the chromic acid estimated by acidifying, adding excess of potassium iodide and titrating with standard sodium thiosulphate solution. The estimation of the acidity of one-bath liquors, which is of great importance, is most conveniently carried out by the method of Procter and M'Candlish.* The whole of the acid is estimated in this way by titration of the boiling diluted solution with normal sodium hydrate with the addition of rather a large quantity of phenolphthalein as indicator.

The colorimetric method forms a useful control of spent one-bath chrome liquors.†

Two-bath Liquors.—The chromic acid in two-bath liquors is estimated by titration with thiosulphate solution in the same way as for one-bath liquors.

Free acid is estimated in two-bath liquors by titration with standard caustic alkali with phenolphthalein.

Since normal chromates are neutral to phenolphthalein, and free chromic acid and bichromates are acid to that indicator, the relative amounts of free chromic acid or of bichromate and chromate may be calculated from the results of the above two titrations.

The thiosulphate in a second-bath liquor is estimated by titrating with it the iodine liberated from potassium iodide by a known volume of an acidified solution of standard potassium bichromate.

Chromium in chrome leather is estimated by ashing a weighed quantity of the leather in a platinum crucible and converting the chromium to chromate by ignition with a mixture of sodium and potassium carbonate. The chromate is dissolved and estimated volumetrically in the usual manner.

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* Procter and M'Candlish, *Journ. Soc. Chem. Ind.*, 1907, 458.
Wood and Law, *Journ. Soc. Chem. Ind.*, 1910, 398.

Two-bath chrome leather may be distinguished from one-bath leather by damping and wrapping in paper with a silver coin. After leaving in a warm place for an hour, the coin will become stained brown or black from the formation of silver sulphide from the sulphur in the leather.

Alum Tannage

The mechanism of the alum-tanning or tawing process is probably the same as that of chrome, the actual tanning agent being regarded as a basic alumina salt.

Small skins which are required to be preserved with the hair or wool on are stretched on a board with the flesh side outwards after cleansing from blood and dirt as far as possible. A strong solution of alum and common salt is applied hot with a sponge, and the application repeated till the skin is struck through. In the manufacture of **glove-kid**, for which lamb skins are used for the most part, and genuine kid skins for the best qualities only, the skins, after liming, puering, and drenching, are treated with a mixture of alum, salt, flour, olive oil, and egg yolks in a thin paste. The mixture is caused to penetrate the skins by being trodden with them or, more usually, by drumming. The goods are then dried rapidly and passed through tepid water and made uniformly moist by treading tightly into chests, in which they remain for twelve hours. They are then trodden on a floor of sharply angular edges formed by bars of wood and subsequently stretched with the "moon-knife" (Fig. 229). The latter consists of a circular knife in the shape of a quoit and is held by the workman by its inner edge and drawn down the flesh side of the skins, which are attached to a horizontal pole by one end, the other being held by the operator. The skins are then dried nearly completely and staked, which consists in drawing them over a blunt knife edge fixed in the top of a post. Staking is also done to a great extent by machine.

The goods are then "aged" from one to three months, which is necessary in fixing the tanning agent and producing the necessary properties of the finished article. They are then dyed after the removal of part of the tawing mixture by treatment with tepid water.

Aniline dyes or natural dyewood colours are used; in the latter case an alkaline mordant is first given, and also usually the colour is made brighter and more permanent by the use of a striker consisting of a salt of zinc, iron, or copper.

The manufacture of **calf kid** is similar to the process just described except that the puering process is omitted, the lime being removed by successive washings and working in the beam.

After drenching, the skins are drummed in the tawing paste, which may consist, according to Procter, of 5 per cent. flour, 2.5 per cent. alum, 1 per cent. salt, the yolks of twenty-five eggs or 1½ lbs. preserved egg yolk, 2 oz. olive oil, and 1¼-1½ gals. of water to 100 lbs. of wet pelt. The skins are penetrated in several hours and allowed to lie in pile overnight and sometimes split, in this condition, in the band-knife machine. They are then dried rapidly and aged for one to three months after damping back and staking by machine. After being thoroughly wetted back, the skins are given an alkaline mordant and blacked with an infusion of logwood or fustic fixed and darkened by a solution of ferrous sulphate. The wetting back causes a loss of part of the tanning material which is replaced by "re-egging" with egg yolk and flour, and sometimes alum and salt. If the goods are blacked on the table the "re-egging" is done previous to dyeing, but if dyed in the tray it is done afterwards, as the dyeing process would result in the removal of a further quantity of the material. After drying again, the goods are softened by staking or perching, and ironed after the application of a composition containing oil and wax, which results in a smooth glossy surface. The process is completed by the application of a final gloss and a small quantity of French chalk.

A large number of processes, combining the use of alum with that of the vegetable tanning materials, are in use.

Dongola leather, which is one of the most important products of these combination tannages, is made by handling the skins in a bath containing gambier, alum, and salt.

"**Green leathers**," largely made in the West Riding of Yorkshire, are first given a light gambier tannage and then handled in a hot and strong solution of salt and alum, and finally heavily stuffed with sod oil.

Oil Tannage

The greater part of the raw material used in oil tannage consists of the flesh split of sheep skins, the finished product being the ordinary "**chamois**" or "**wash leather.**" The skins are split after the completion of the liming process, and the loose and fatty middle layer is removed by a sharp knife on the beam ("frizing"). Part of the lime in the goods is then removed by means of drenching (see p. 581). After draining, as much as possible of the water is removed, either by stocking with sawdust in the fuller stocks or by hydraulic pressing. By this means the fibre is isolated and opened out and the skin rendered porous and easily able to absorb the oil. The goods are then placed again in the fuller stocks (Fig. 228) and cod oil added in small quantities at a time and evenly distributed by the motion of the skins. They are then hung to allow evaporation of the remaining water and penetration of the oil. Care is necessary to avoid any part of the skin drying before absorption of the oil, or hard and transparent patches will result. The processes of oiling, stocking, and hanging are repeated till all the water previously in the skins has been replaced by oil. The goods are then hung in "stoves" heated to a high temperature in which large quantities of irritating vapours are produced by the oxidation of the oils. The oxidation is carried further in the English method by packing the skins in large boxes or tubs in which great heat is spontaneously generated, which would destroy the goods if allowed to proceed. When the maximum temperature, which the skins will safely stand is reached, the goods are removed from the boxes and strewn on the floor to cool. They are then replaced in the receptacles and the process repeated till oxidation is complete and no further heating occurs. In the French method the oxidation is completely effected in the stove without the use of the packing process.

The goods are then dipped in water and wrung or hydraulically pressed, and the excess of oil thus removed constitutes moellon, dégras, or sod oil, which is an extremely valuable material for use in currying, so much so that skins are frequently oiled and pressed for the sole purpose of obtaining it.

A further quantity of sod oil of an inferior quality is obtained from the pressed leather by paddling with soda or potash solution and recovering the oil by decomposing the soap thus formed by acidification with sulphuric acid.

Buff leather, for military accoutrements, is made in a similar manner from hides after removal of the grain by frizing. Bleaching of buff and chamois leather is effected by exposure in a damp condition to sunlight, or by means of oxidising agents.

A similar product, obtained without the use of oils, is the "**Kaspine**" leather of Messrs J. & E. Pullman.* The goods, prepared as for oil tannage, are treated in a drum with a very dilute solution of formaldehyde rendered alkaline with sodium carbonate. The product is very similar to oil-tanned leather, but needs no bleaching, being white right through.

Various other methods of employing oils and fats in the tanning of leather are in use, of which the "**Crown**" and "**Helvetia**" leathers are the most important products. The method of manufacture of the former, originally devised by Klemm, consisted in treating the prepared skins with a mixture of flour, ox-brains, butter, milk, and soft fat, and drumming in warm drums.

"**Riems**" are made in South Africa by cutting a strip of raw hide, and suspending with a heavy weight on one end after coating with oil. By repeated oiling and twisting the thong is saturated with the oil, and an extremely tough and flexible leather is produced.

Artificial leather, a product of recent years, is made by separating into their constituent fibres such substances as waste leather, cotton, paper, felt, etc. (as under **Paper**), then oiling the fibres to render them soft, and cementing them together by kneading with a solution of celluloid, viscose, or caoutchouc in special machines, drying and calendering. The product is used for furniture-covering, stiff wallpaper, and ornamental articles such as cheap ladies' bags, purses, etc.

Pergament, or parchment, is not true leather, but consists of calf skins and the flesh splits of sheep skins well rubbed with pumice stone and chalk paste, and dried in a stretched condition. It forms a horny substance, lacking the flexibility of leather; in a damp condition it may putrefy.

* English Patent, 2,872, 1892.

SECTION XX

The Glue, Gelatine, and Albumen Industry

THE GLUE, GELATINE, AND ALBUMEN INDUSTRY

By G. Martin, Ph.D., M.Sc.

GLUES AND GELATINE

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Ordinary glue is a product of decomposition of nitrogenous matter contained in animal skins and bones. When hides are heated with water they swell up, lose their organic structure and dissolve to a clear solution, which on cooling—even when it contains only 1 per cent. of nitrogenous matter—solidifies to a jelly ("gelatine") and dries to a transparent mass, known as glue. The dried mass will again dissolve in hot water, giving a solution which has an extraordinary adhesive capacity.

Three main varieties of glue are manufactured: (1) **Hide Glue**; (2) **Bone Glue**; (3) **Fish Glue**.

All these kinds of glue have approximately the same composition (C=49-51 per cent., H=6.5-7.5 per cent., N=17-18.8 per cent., S=0.7 per cent.) and consist of a mixture of protein-like substances, the chief constituent of which is called "**Glutin**." Glutin has not yet been obtained quite pure, and is an amorphous, tasteless, and odourless substance, which swells up in cold water and passes into a colloidal solution in hot water; it is precipitated from aqueous solution by alcohol and also by tannic acid, the latter uniting with it to form an insoluble compound, probably connected with the insoluble body produced in tanning leather (see **Leather**).

Formaldehyde also renders gelatine and glue insoluble. Alum and ferrous sulphate in the presence of alkali precipitate glutin.

When glutin is boiled with water for any length of time it undergoes further decomposition, yielding products very deficient in adhesive capacity and incapable of forming jellies (see p. 568).

Manufacture of Hide Glue

Fresh waste from tanneries and slaughter-houses (scraps of hide, earlaps, tails, tendons, feet of oxen and sheep, etc. etc.) is placed in cemented vats filled with thin milk of lime and left for three weeks or less. The lime saponifies fatty matter (forming insoluble calcium soaps and glycerol), and partially dissolves non-gluey matter, such as blood, flesh, coriin, thus making the hide loose and soft. Next, the material is freed from traces of lime (otherwise the product will be inferior) by careful washing and by treating with acid solutions, *e.g.*, dilute sulphurous acid or spent tan liquor. Sometimes instead of liming a treatment with SO_2, followed by bleaching with bleaching powder, is followed.

The raw product thus obtained is rinsed and then boiled with the proper amount (not too much) of water in open tinned pans, usually provided with a false sieve-like bottom and heated by steam coils or a steam jacket. The glue dissolves in the warm water, but hair and meat remain suspended. The fats and calcium soaps float to the surface and are skimmed off. Long boiling must be carefully avoided as it injures the glue. When solution is complete the liquid is filtered off as clear as possible through the sieve bottoms and run into a vacuum pan and is concentrated at 60° C. (see Fig. 21, p. 81, for a type of the vacuum pan employed). Higher temperatures seriously damage the sticking power of the glue owing to partial decomposition of the glutin. The lower the temperatures used the better the glue. When the concentration reaches 15-20 per cent., the yellow dirty-looking fluid is partially clarified by SO_2 or other clarifying agent.

Complete decolourisation is usually not possible even by the combined action of SO_2 and animal charcoal. Great care must be taken in the use of decolourising agents since they usually seriously damage the glue. Alum, for example, renders much of the glue insoluble, and affects its adhesive properties.

When the proper degree of concentration is attained the glue is poured in a thin layer about $\frac{1}{3}$ in. thick over large, flat, smooth surfaces usually consisting of surfaces covered with glass plates cooled below by cold water. The glue is thus rapidly cooled and sets to a gelatine. It is then cut up into tablets of convenient size, and rapidly dried at as low a temperature as possible. If the drying is not rapid enough putrefaction may set in, as gelatine is an excellent developing medium for bacteria; if the temperature of drying is too high the gelatine melts. The gelatine tablets are therefore usually laid on netting (its impression showing on the finished article), and dried in a draught of air at 20° C. in special chambers. The tablets thus produced contain about 15 per cent. of water, and a considerable amount of ash. The less the glue has been boiled and the thinner the plates the better the adhesive properties of the product. The value of a glue is tested by actual trial, the chemical analysis having little value as a criterion of its adhesive quality.

Many attempts have been made to use tanned leather or leather wastes for glue making, but with somewhat doubtful success in most cases. Such leather is "untanned" by treating first with alkali, and then with lime. Chrome leather is untanned by dipping in dilute H_2SO_4, rinsing with H_2O, and neutralising with lime. The last traces of lime are removed by HCl, then alkali, and the product is finally washed and boiled for glue.

Trotman (British Patents, Nos. 5,676, 12,393, 1911) degromes chrome tanned leather for the preparation of glue by treating with dilute HCl or H_2SO_4, washing, neutralising with alkali, and treating with sodium peroxide which converts the chromium compounds into chromates, which are then removed by washing. The amount of NaOH present is controlled by adding $CaCl_2(2NaOH + CaCl_2 = 2NaCl + Ca(OH)_2)$. Trotman detans ordinary tanned leather by soaking in alkali, rinsing, treating with sodium peroxide, rinsing, and neutralising with acid.

Manufacture of Bone Glue

This is prepared by several processes.

(*a*) **Acid Process.**—The bone is soaked in an 8 per cent. solution of HCl which extracts the mineral matter (calcium phosphate). The stiff cartilage remaining is washed with lime water and dissolved in boiling water as described under Hide Glue.

The acid solution of calcium phosphate is neutralised with milk of lime, and gives a precipitate of calcium phosphate, which is used for making manures or as a source of phosphorus. A yield of bone fat is also obtained.

Yield.—100 parts of bones give 16 glue, 35 calcium phosphate precipitate, 8 fat.

The glue thus obtained is equal in every respect to hide glue. The acid, however, render the process somewhat expensive, consequently sulphurous acid

under pressure has been used instead of HCl for extracting the mineral matter—a method which economises the acid and prevents the formation of an insoluble crust of calcium sulphite, which otherwise greatly retards solution.

Among other suggested improvements, German Patent, No. 166,904 purifies glue by dissolving it in warm $MgSO_4$ solution and precipitating with HCl; German Patent, No. 168,872 uses monochloracetic acid for extracting glue from bones, while German Patent, 177,625 uses dil. ammonia for the same purpose. German Patent, No. 187,261 bleaches glue by heating to 100° C. with the basic zinc salt of formaldehydesulphoxylic acid.

(*b*) The ordinary method is to first extract the bones with benzine or other solvent, thus obtaining the bone-fat (see under **Fats**). Steam is driven through the extracted bones to expel all solvent; the bones are then washed in rotating drums to cleanse them from dirt, flesh, etc. Next the bones are coarsely broken, placed in four iron cylinders and treated several times in succession with steam under 2 atmospheres pressure and with boiling water. The steaming has a disintegrating effect which renders the solution of the glue by the water more easy. When most of the nitrogenous matter has been extracted by the water, the bones (which should now contain less than 1 per cent. N) are ground up and used as manure (bone meal). The glue solutions are evaporated in vacuum pans as above described.

Since the mineral matter is closely united with the protein material of the bone, the glue is far more difficult to dissolve out from bones than from hides; consequently this kind of bone glue, which has been produced with a considerable amount of boiling, is not so good as the hide glue or the glue produced from bones by the acid process. Putrefying bones also yield an inferior product.

Fish Glue

This is produced from fish scales and skins, also from fish heads and bones (especially cod) by treating with HCl, washing, liming, and boiling with water. The manufacture is carried out as with other glues, but alum is often used for decolourising. Isinglass is the purified and dried inner skin of the sturgeon's swimming bladder. Glue has been manufactured from whale blubber (German Patent 131,315) by extracting the oil first by cold pressing, then by extracting with benzol; the glutinous membrane remaining, dry and entirely fat-free, is then worked for glue.

Fish glue is used by cabinetmakers, and when properly made is as good as other kinds. Usually, however, it is deficient in adhesive power.

Uses of Glue.—Glue is used extremely widely for many very different industrial purposes, *e.g.*, for sizing special kinds of paper (drawing); in the hat industry; for finishing special kinds of woven material, especially silken netting; in joinery for cementing together wooden joints; in the printing industry for making printers' rollers, which consist of glue and glycerin or glue and treacle, forming an elastic, non-sticky and durable surface. In the colour industry paints are manufactured by rubbing up colouring matters with a solution of glue. In modelling and stuccato work a solution of glue is mixed with the plaster. "English Plaster"—used for wounds and cuts—consists of fine netting painted over with a solution of isinglass in alcohol. Cements for glass and porcelain usually consist of glue and mastic, or some similar resin, dissolved in alcohol. In the match industry very large amounts of glue are used as binding material.

Testing Glue.—The strength of a glue is usually tested by gluing pieces of dry clean wood together and ascertaining the force required to break the joint. Estimation of glue by precipitating with tannic acid is quite useless.

Gelatine

Is a very pure colourless and odourless glue obtained either from calves' heads or the cartilage and skins of young animals, only the first extracts being used with the best sorts, and concentration by evaporation being avoided. The raw material must be quite fresh and very thoroughly cleansed; the glue solution is carefully clarified, being bleached with sulphurous acid. Gelatine for photographic purposes must be especially pure, since the slightest trace of putrefaction causes the generation of reducing compounds which act on silver or gold salts in the film. Such gelatine is prepared from the head and leg portions of calves, which are useless for leather manufacture; gelatine prepared from skin tissues has a great power of coagulation.

Gelatine is usually made in the form of very thin leaves (to facilitate rapid drying). They are frequently dyed with coal-tar colours; sugar and alcohol added make gelatine more flexible. Gelatine is now produced as threads, as a powder, and in thick plates.

Uses.—Gelatine is largely used as a food for making jellies, puddings, etc., for which purpose it is delicately coloured and mixed with sugar and flavouring materials. In photography it is largely used for preparing negatives, films, etc. Also for heliographical printing, the process depending upon the fact that if a plate covered with a mixture of gelatine and potassium dichromate is exposed to light, the illuminated portions become insoluble, while portions in the shade remain soluble; hence on washing the plate printable pictures are obtainable; formaldehyde also renders gelatine insoluble, and is used for making photographic films, vessels, ornaments, spangles for dresses, etc. The gelatine capsules used in medicine consist of gelatine and glycerol. In bacteriology gelatine is used as a transparent nutrition medium for cultivation. Fishing nets and sails are often coated with warm gelatine and then immersed in a concentrated solution of tannin, which renders the gelatine insoluble and preserves the fishing nets against the attacks of destructive organisms.

Gelatine is also used for removing turbidity from liquors such as beer and wine—which contain tannic acid. **Isinglass** (fish gelatine, consisting of the dried inner skins of the swimming bladder of the sturgeon and similar fish) is also much used for clearing and similar purposes, but is now being gradually displaced by gelatine.

Gelatine, isinglass, and other fish-bladder glues have only a very feeble adhesive power.

A vegetable gelatine is yielded by *Agar-agar*, a seaweed of the East Indies. It is nitrogen-free, consisting of carbohydrate.

Glutol or **Glutoform** is formaldehyde gelatine, prepared by evaporating a gelatine solution with formaldehyde or treating gelatine leaves with formaldehyde. Insoluble in hot water. Used as an antiseptic powder.

Liquid Glue

When a solution of glue is mixed with acetic, nitric, or hydrochloric acid, or heated with zinc chloride, the glue still retains its power of sticking, but has lost its power of gelatinising. The following are some well-known receipts: 100 parts glue are dissolved in 110 parts boiling water, and 40 parts of nitric acid of 35° Bé. are added. 12 parts glue + 32 parts H_2O + 2 parts HCl + 3 parts $ZnSO_4$. Warm ten to twelve hours at 80°-85° C.

"**Liquid Glue**" is usually **dextrin** (which see) or of vegetable origin (see **Gum Arabic**, p. 346).

Marine Glue consists of india-rubber (1 part) dissolved in turpentine or paraffin (12 parts), to which are added 2 parts asphalt or shellac. A powerful waterproof adhesive; must be applied hot. Another recipe is: add 30 parts finely divided rubber to 2 parts melted tallow; melt carefully and stir in 2 parts lime or minium.

Casein Cement is made by mixing fat-free fresh casein (cheese) with milk of lime. It must be used immediately. It is a powerful cement much used by joiners, bookbinders, etc., also for cementing glass and porcelain (see **Industrial Casein**, p. 79).

For other **adhesives, gums**, etc., see under **Dextrin, Gum Arabic**, etc.

Statistics.—England *imported* in 1910 of glue, size, and gelatine, 246,500 cwt. (value £472,500); gluestock, 175,200 cwt. (value £120,120); isinglass, 10,400 cwt. (value £109,800).

The glue export amounted to 300,300 cwt. (value £242,500).

The yearly sale of glue in the United States amounts to about $12,000,000. The United States imported in 1910 73,400 cwt. of glue (value $862,000); gluestock of value $1,605,000; gelatine 11,100 cwt. (value $387,000); isinglass, 3,000 cwt. (value $76,000).

The United States export of glue was 28,200 cwt. (value $299,000) in 1906, and 22,000 cwt. (value $262,000) in 1910.

INDUSTRIAL ALBUMEN

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Two varieties of albumen are now on the market, viz., egg albumen and that derived from blood serum. They have different properties.

Egg Albumen

The approximate composition of egg albumen is: Water, 84 per cent.; dry albumen, 11.9; fats, etc., 3.6; ash, 0.5 per cent.

Properties.—Egg albumen coagulates at 72°-73° C. In a 1 per cent. solution albumen coagulates at 56° C. The sp. gr. is 1.0026 for a 1 per cent. albumen solution, and 1.0515 for a 15 per cent. Albumen is precipitated from solution by alcohol, tannic acid or tannin, lead acetate, metaphosphoric acid, etc.

Albumen combines with acids to produce acid albumens, and with bases to produce alkali albumens. It also unites with halogens—in fact it is a very reactive substance. All these compounds are unstable.

When dried, albumen will keep almost indefinitely. Moist albumen soon putrefies.

Manufacture.—The eggs are broken, separated from the yellow yolk without mixing, the albumen strained through silk gauze lining the lead-lined drums of centrifugal machines, allowed to settle for thirty to forty hours (or cooled five to six days to a low temperature in iron vessels), when the albumen should be quite clear. Some firms clarify by a little tannin or acetic acid and turpentine oil and pressure through a Vollmersch filtering apparatus. The clear albumen is then dried as rapidly as possible in a stream of dry air or *in vacuo* (see Fig. 21, p. 81, in **Condensed Milk**) *under* 50° *C.* (above this temperature the albumen becomes yellow) for about four to six hours, when it is obtained as thin clear elastic sheets; 230-300 eggs yield 1 kg. dry albumen. With water it dissolves to a perfectly clear odourless solution.

Industrial **Lecithin** (yolk powders) is made from the egg yolks above separated. The Lecithin forms a pasty mass which is absorbed in wheat protein, and sold as a component of invalid foods and for other purposes. **Lecithin** is a compound of **choline, glycerol, phosphoric** and various fatty acids, and occurs in the brain-substance, bile, and blood. It has great medicinal value. For methods of extraction see *German Patents*, Nos. 200,253, 210,013, 223,593, and *French Patents*, Nos. 371,391, 390,683.

Blood Albumen

The freshly caught blood is spread in shallow dishes and when the separation into fibrin and pale yellow serum is complete, the latter is treated like egg albumen (above). To obtain the albumen quite pure the serum is forced through charcoal filters, the albumen precipitated with lead acetate, washed, and the lead albuminate decomposed with CO_2, settled, the lead removed by H_2S and filtered, and the albumen evaporated *in vacuo* as above described. 1 kg. serum albumen requires the blood of 2.5 cows, 10 sheep, or 17 calves. For various improvements see English Patent 10,227, 1905, and German Patents 137,994, 143,042.

Uses.—As a mordant in dyeing and calico printing; in the manufacture of gums and adhesives; as a clarifying agent; for the preparation of photographic papers; in medical foods.

Statistics.—The German import in **dried albumen** amounted in 1910 to 612 tons, in value £125,000: the majority came from China. The English import in 1910 amounted to £21,767.

The United States in 1910 imported 88 tons (value $29,000) of blood albumen; 312 tons (value $269,000) of egg albumen; and 3½ tons of unspecified albumen (value, $1,200).

SECTION XXI

The Industry of Modern Synthetic and other Drugs

THE INDUSTRY OF MODERN SYNTHETIC DRUGS

By F. Challenger, Ph.D., B.Sc.

LITERATURE

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" "Die Alkaloidchemie in den Jahren 1900-1911." 3 vols.

For the Patent Literature up to 1905 see Winther's "Patente der Organischen Chemie." 877-1905. 3 vols. For **Trade Names** of the newer drugs, see list on p. 667 (Appendix II.).

INTRODUCTION

It is impossible in the space at our disposal to give a complete account of the enormous number of new drugs now on the market. The reader is referred to the above-mentioned literature for further information. All that is attempted is a brief account of some of the more important of the drugs—especially the newer synthetic ones—which within the last few years have been placed on the market, and which will in the future play an important part in therapeutics.

The larger modern chemical firms—such as Burroughs Wellcome & Co.; Merck; Meister, Lucius, & Brüning—employ a staff of university-trained scientists to synthesise and test new drugs, and some of the recent discoveries made by these firms are certainly epoch making. The whole chemistry of Ergot, for example, has been revolutionised by recent work carried out in the laboratories of Messrs Burroughs Wellcome & Co. by Barger and others, while equally important work has been done by Meister, Lucius, & Brüning of Höchst on Adrenaline and on the new organic arsenic compounds used in treating sleeping sickness and syphilis.

Statistics.—The following figures show the magnitude of the import and export of drugs into the United Kingdom :—

IMPORT.

	1906.	1913.	Value, 1913.
Opium	825,836 lbs.	566,834 lbs.	£507,261
Quinine and quinine salts	1,973,039 oz.	2,422,944 oz.	102,101
Peruvian bark	24,602 cwt.	26,122 cwt.	58,000
Chloral hydrate	19,978 lbs.	23,501 lbs.	2,080
Chloroform	972 ,,	1,366 ,,	347
Other drugs and medical preparations	...	...	1,302,800
Total	...	...	£1,972,589

The amount of imported tea for the manufacture of **caffeine** was 1,500,000 lbs. (value £10,300) in 1913.

EXPORT.

	1906.	1913.	Value, 1913.
Cocaine	...	3,300 oz.	£1,000
Morphia	...	400,000 ,,	193,000
Opium	...	12,100 lbs.	12,400
Quinine and quinine salts	1,059,948 oz.	1,374,000 oz.	72,600
Other medicines and drugs	...	...	2,072,000

The United States imports (entered for consumption) in 1910 were :—

	Quantity.	Value.
Caffeine	60,500 lbs.	$100,500
Chloroform	960 ,,	1,500
Cinchona bark	3,300,000 ,,	242,000
Quinine sulphate, quinine, and other alkaloids from cinchona bark	3,000,000 oz.	398,000
Cocaine	29,600 ,,	38,000
Cocaine salts, ecgonine	24,900 ,,	42,000
Ergot	181,600 lbs.	53,000
Ichthyol	14,400 ,,	21,500
Iodoform	31 ,,	97
Opium	439,000 ,,	1,575,000
Morphia and salts	13,000 oz.	60,000
Other opium alkaloids	23,000 ,,	66,000
Santonin and salts	7,300 lbs.	53,000
Strychnine and salts	2,000 oz.	1,000

ANÆSTHETICS

Anæsthetics may be divided into (*a*) General Anæsthetics, (*b*) Local Anæsthetics.

(*a*) General Anæsthetics

Produce total insensibility to pain. Usually administered by inhalation. The most important are :—

Chloroform, $CHCl_3$.—For manufacture and properties see p. 377. For anæsthetic purposes it should contain 1 per cent. absolute alcohol, or it undergoes

decomposition. Used for operations where a considerable interval of anæsthesia is required.

Ether, $C_2H_5.O.C_2H_5$.—For preparation and properties see p. 381. Anæsthesia endures for a shorter time than that produced by chloroform.

Ethyl Chloride, C_2H_5Cl.—Obtained by passing dry HCl gas into ethyl alcohol in the presence of $ZnCl_2$ (see p. 377). B.P. 12.5° C., hence is gaseous at ordinary temperatures. Miscible with alcohol. Sparingly soluble in H_2O. Produces anæsthesia in 30 to 120 seconds, which endures for fifteen to twenty minutes. Only one nineteenth the paralysing action on the heart of that possessed by chloroform.

Ethyl Bromide, C_2H_5Br.—Now produced very pure by Merck. Colourless liquid of B.P. 38.4° C.; sp. gr. (13° C.) 1.47. Produces extremely rapid anæsthesia, but has a somewhat irritating action on the lungs.

Narcotil is a mixture of methyl and ethyl chlorides.

Somnoform consists of the same ingredients with the addition of **ethyl bromide**.

(*b*) Local Anæsthetics

There is a large and increasing number of organic compounds which, under suitable conditions, can render certain definite portions of the body insensible to pain ("local anæsthesia"). Certain alkaloids, for example, when dropped upon the eye in the form of solution, render possible operations which would otherwise have to be performed under the influence of chloroform or one of the other general anæsthetics. Similarly, when such a substance is injected at the base of the spine, the whole of the region of the loins is rendered completely insensible to pain.

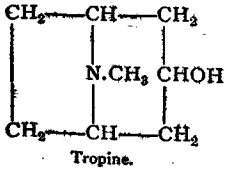
The discovery of the action of these drugs is one of the very greatest importance to the medical man, and during the last ten years they have almost superseded chloroform for the performance of several of the less serious operations. Moreover, in cases where, for several reasons, it is not yet considered advisable to dispense with the use of a general anæsthetic, the quantity of the latter which is required has been considerably reduced by administering a local anæsthetic as well. This is of special importance in cases where, owing to certain diseased conditions of the organism, the use of chloroform is attended with more than the usual amount of danger.

Most of these drugs are administered by injection into the region which it is desired to anæsthetise. For operations upon the eye, the solution is usually applied in the form of drops.

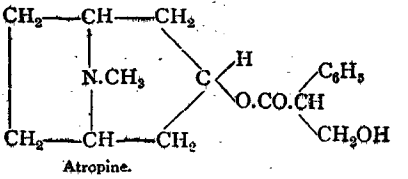
The chief local anæsthetics employed are:—

Cocaine, $C_{17}H_{21}NO_4$, a white crystalline alkaloid occurring in the leaves of *Erythroxylon coca* of Bolivia and Peru. The leaves contain 1 per cent. ether soluble alkaloids, about half of which is cocaine, the other alkaloids including tropacocaine, truxilline, cinnamylcocaine, and hygrine. The leaves are exhausted with water at 60°-80° C., protein matter precipitated with lead acetate, excess of lead removed by Na_2SO_4, the filtered solution concentrated, made alkaline with ammonia, and the alkaloid extracted with ether.

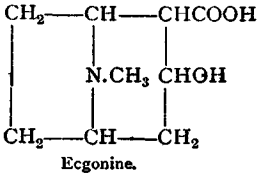
Cocaine is methylbenzoylecgonine, ecgonine being a carboxyl derivative of tropine. Its relationship to atropine, the alkaloid of *Atropa belladonna* or the Deadly Nightshade, will be seen from the constitutional formulæ:—

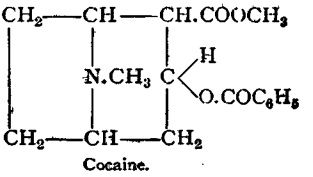


Tropine.



Atropine.


Ecgonine.


Cocaine.

Other alkaloids, with very undesirable action, which occur in the coca leaves, may be converted into ecgonine by heating with HCl. Pure cocaine can then be prepared synthetically from ecgonine.

Properties.—Large colourless crystals, M.P. 98° C.; bitter taste; very sparingly soluble in water; soluble in alcohol, ether, benzene, chloroform, etc. Forms monovalent salts with acids.

In small doses the drug sustains muscular energy, raises the body temperature and blood pressure. Dilates the eye pupil. Excess causes death by convulsions. Its chief value is its power of paralysing nerve-ends, and so causing local anæsthesia for minor surgical operations. Maximum daily dose, 0.15 g.; maximum single dose, 0.05 g. For injections a 5-10 per cent. solution is used.

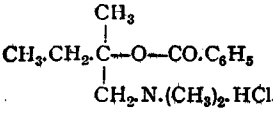
Tropacocaine = benzoyl-ψ-tropine, $C_{15}N_{19}NO_2$. Accompanies cocaine in the leaves of *Erythroxylon coca*; sixty-three times less toxic than cocaine, and its action commences more quickly. No dilation of the pupil. It is an excellent local anæsthetic, and is coming more and more into use.

Synthetic substitutes for **cocaine** are:—

Anæsthesine, $NH_2.C_6H_4.COOC_2H_5$.—Obtained by reducing *p*-nitrobenzoic ethyl ester with Sn + HCl. Excellent anæsthetic of low toxicity and non-irritant power. Used for anæsthising wounds and checking vomiting.

Novocaine, $NH_2.C_6H_4.CO_2.CH_2.CH_2.N(C_2H_5)_2,HCl$. — Excellent local anæsthetic, used in dentistry, and for the production of spinal anæsthesia. Often used with adrenaline.

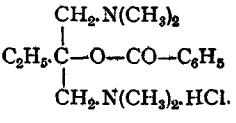
Stovaine forms white, lustrous scales, M.P. 175°, readily soluble in water; prepared by the interaction of magnesium ethyl bromide and dimethylaminoacetone, and subsequent benzoylation of the product thus formed. It has the constitution:—



As little as 0.3 c.c. of a 10 per cent. solution are sufficient to produce anæsthesia in the legs below the knees.

Much used as a local anæsthetic in dental, ophthalmic, and minor surgical operations. Much less toxic than cocaine.

Alypine has the constitution



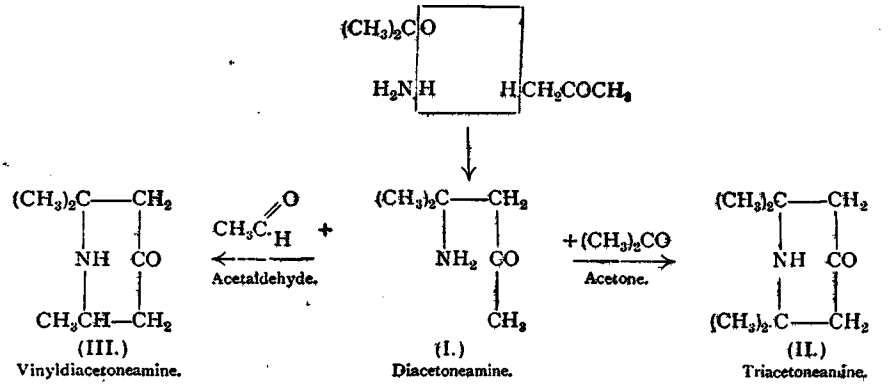
Readily soluble in H_2O and probably superior to stovaine as a local anæsthetic. Used as a substitute for cocaine in 1-5 per cent. solution.

When administered along with heroine (diacetylmorphine) the demulcent and sedative effects of the latter drug are enhanced, and the combination has proved very successful in allaying the nocturnal cough of pulmonary tuberculosis.*

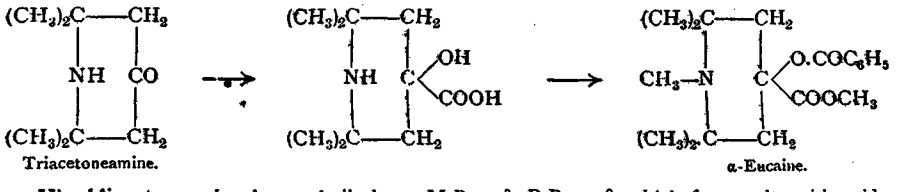
The Eucaines.—The important results which usually follow the determination of the chemical constitution of any important physiologically active substance are well instanced by the existence of α- and β-eucaine.

The preparation of these two compounds was a direct outcome of the various attempts which were made to prepare substances chemically related to cocaine.

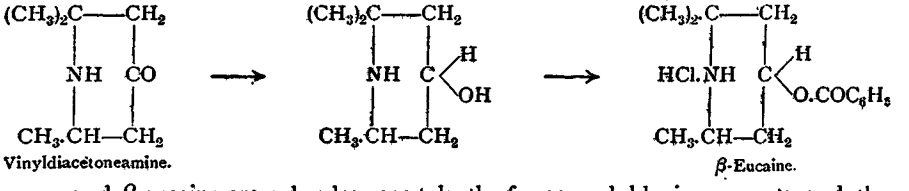
Preparation of the Eucaines.—By the condensation of 2 molecules of acetone with 1 of ammonia, diacetoneamine is formed (I.). If this be allowed to react with a third molecule of acetone, the symmetrical triacetoneamine is obtained (II.). If instead of allowing the diacetoneamine to react with acetone, acetaldehyde be used, the product is a substance known as vinyldiacetoneamine (III.). Thus:—



Triacetoneamine is a crystalline solid, M.P. 39°-40°. It has a strong alkaline reaction and its odour is ammoniacal, and also similar to that of camphor. When converted into its cyanhydrin, and then hydrolysed, methylation and benzoylation of the resulting hydroxy acid yield α-eucaine.



Vinyldiacetoneamine is a volatile base, M.P. 27°, B.P. 200°, which forms salts with acids. When the carbonyl group in this substance is reduced, benzoylation yields a derivative, the hydrochloride of which is β-eucaine.



α- and β-eucaine are colourless crystals, the former soluble in 10 parts and the latter in 30 of water. α-Eucaine has been abandoned in practice owing to its irritant action on the tissues.

The anæsthetic action of β-eucaine is somewhat feebler than that of cocaine, and in consequence of its vasodilatory properties it gives rise to hæmorrhage and causes pain when injected. It has also a tendency, when used in ophthalmic surgery, to cause hardening. This difficulty seems to have

* Laufer, "Merck's Reports," 1907, 21; *Reichs-Medizinal-Anzeiger*, 1907, 17.

been largely overcome by Langgaard * by combining β-eucaine with lactic acid, when a product is obtained which is non-irritant and causes neither local anæmia, hyperæmia, nor shrinkage. Injections of β-eucaine have been employed by Opitz † with very great success in the treatment of sciatica and neuralgia, the drug having a decided curative as well as analgesic effect.

In spite of the similarity in chemical constitution between the eucaines and cocaine, they are hardly such satisfactory substitutes for the latter drug as tropacocaine.

SYNTHETIC ANTIPYRETICS

Acetanilide, or Antifebrin, $C_6H_5.NH.COCH_3$, prepared by heating in earthenware vessels for one to two days equal parts of aniline and glacial acetic acid: $C_6H_5.NH_2 + CH_3.COOH = H_2O + C_6H_5.NH.CO.CH_3$.

Used as a febrifuge in cases of typhoid fever, small-pox, phthisis, rheumatism, and erysipelas. Prolonged use is dangerous.

Acetylsalicylic Acid (Aspirin), $C_6H_4(CO_2.CH_3).CO_2H$, prepared by heating salicylic acid with acetic anhydride or acetyl chloride, and recrystallising from chloroform. See also American Patent 749,980 and English Patent 15,517/02. White needles, M.P. 135°. Moderately soluble in water, easily in alcohol and ether. Dose, 0.5 g.; 4 g. may be given daily for rheumatism and neuralgia.

Phenacetine is acetyl *p*-phenetidine, $C_6H_4\begin{matrix}O.C_2H_5\\NH.CO.CH_3\end{matrix}$ *Preparation.*—

Phenol, C_6H_5OH, is nitrated, and the *p*-nitro-phenol, $C_6H_4.(NO_2).OH$, is separated from the *o*-compound, and ethylated with ethyl sulphate, whereby $C_6H_4(NO_2).OC_2H_5$ is produced. This is reduced with Sn + HCl, thereby producing **Phenetidine,** $C_6H_4(NH_2).OC_2H_5$, which is then acetylated by boiling with acetic acid, thus producing phenacetine, $C_6H_4.(OC_2H_5).NHCOCH_3$. White crystals; tasteless; valuable antipyretic and antineuralgic. Dose, 0.5-0.75 g. Very largely used, England importing about 8½ tons yearly. Owing to its sparingly soluble nature its action takes place slowly. This defect is partially overcome by introducing an NH_2 group into its acetyl group, thus producing **Phenocoll.**

Triphenine is propionyl-*p*-phenetidine, $C_6H_4(OC_2H_5)NH(CO.CH_2.CH_3)$, prepared similarly to phenacetine by heating *p*-phenetidine with propionic acid. Very sparingly soluble in H_2O. M.P. 120° C. Antipyretic and antineuralgic.

Phenocoll, $C_6H_4(OC_2H_5).NH.CO.CH_2.NH_2$.—It is prepared by acting on phenetidine with chloracetyl chloride, and treating the resulting compound with ammonia; its salts are soluble in water. It is a rapidly acting antipyretic and antineuralgic, but is transitory in its effects.

Neraltein, a new drug, is the sodium salt of *p*-ethoxyphenylaminomethanesulphonic acid; white crystals, soluble in 10 parts of cold water.

C_2H_5O NH.$CH_2.SO_2ONa + H_2O$.

Only slightly toxic, and in small doses produces no irritation of the kidneys; possesses good analgesic properties, and has been used in slight cases of rheumatism.

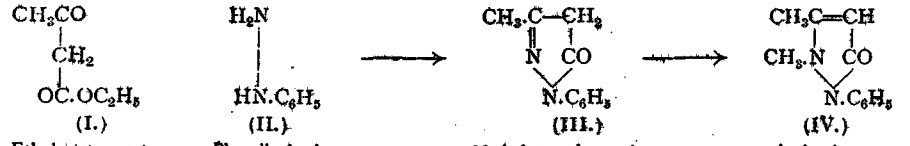
Antipyrine is the most important member of the "pyrazolone drugs."

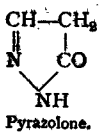
Manufacture.—Phenylhydrazine (II.) (216 parts) is dissolved in dilute sulphuric acid (300 g. of acid in 2 l. of water). Ethyl acetoacetate (I.) (260 parts) is then allowed to flow into the solution at a temperature of about 40°, the mixture being stirred constantly. After the reaction is at an end, excess of caustic soda solution is added and the mixture extracted with ether. From the ethereal extract, after washing with caustic soda solution and drying over calcium chloride, methyl-phenyl-pyrazolone (III.) is obtained as an oil which can be distilled *in vacuo*.

When 200 parts of this are heated with 140 parts of methyl iodide and 200 parts of methyl alcohol at 100°-110° for twelve hours, methylation takes place. After removing the alcohol by evaporation

* "Merck's Reports," 1904, 63; *Therapeutische Monatshefte*, 1904, No. 8, 416.
† *Ibid.* 1907, 97; *Klinisch-therapeutische-Wochenschrift*, 1907, No. 14.

the residue is decolourised with a little dilute solution of sulphurous acid. Caustic soda is then added and the precipitated oil extracted with benzene from which solvent the drug can be crystallised.





Pyrazolone.

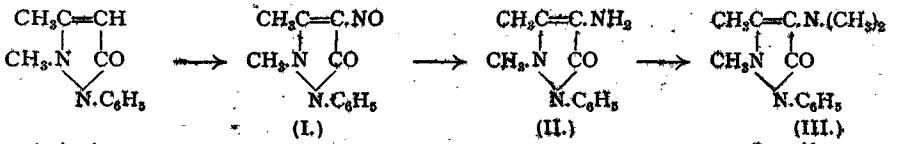
Antipyrine (IV.) forms colourless, inodorous, scaly crystals possessing a bitter taste; readily soluble in water, chloroform, or alcohol. M.P. 112°-113°. Acts as a base forming salts directly with acids. Much valued for the treatment of fever, neuralgia, and rheumatism. Dose, 0.25-2 g. daily.

Tussol—prescribed for whooping cough—is the antipyrine salt of Mandelic acid.

Migräneine is a mixture of caffeine citrate and antipyrine, used for headaches, etc., as an antipyretic and antineuralgic.

Salipyrine is antipyrine salicylate.

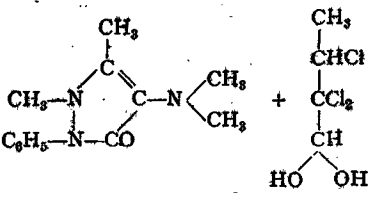
Pyramidone, 4-dimethylamino-antipyrine, is prepared from antipyrine hydrochloride by the action of nitrous acid whereby a nitroso-antipyrine is produced (I.). On reduction this is converted into aminoantipyrine (II.) which is isolated in the form of its benzylidene derivative. On treatment with methyl iodide it yields pyramidone (III.). This forms small colourless crystals of slightly bitter taste which are readily soluble in water. M.P. 108°.



Pyramidone possesses advantage over antipyrine in that it may be prescribed in cases where there is cardiac weakness. The effective dose is only one-third that of antipyrine while it has no irritant effect on the stomach or kidneys.

It has been largely used to allay the high temperatures of typhoid fever and of phthisis, and also in neuralgia and rheumatism.

Trigemine is dimethylaminoantipyrine + butyl chloral hydrate, $C_{17}H_{24}O_3N_3Cl_3$, or :—



It is prepared by mixing dimethylaminoantipyrine with butyl chloral hydrate. M.P. 85°. Soluble in H_2O, alcohol, and benzene; less so in ether and ligroin. Has an analgesic effect, and is prescribed for headaches, neuralgia, etc. Mild antipyretic. Dose, 0.5-1.2 g.

HYPNOTICS

An ideal hypnotic will produce a normal sleep as differentiated from a **narcotic** which produces unconsciousness by intoxication.

The first hypnotic used was **Chloral Hydrate**, $CCl_3.CH(OH)_2$ (1869), the manufacture and properties of which are treated on p. 379. Chloral hydrate, while producing sleep, exerts a depressing action on the heart, sometimes acts as a toxic agent, and often sets up the "chloral habit." Consequently a large number of substitutes have been sought.

Dormiole is amylene chloral, $CCl_3.CH(OH).O.C_5H_{11}$, produced by mixing 6 parts amylene hydrate + 10 of chloral. Colourless oily liquid, insoluble in water, soluble in alcohol, ether, acetone, etc. Useful and harmless soporific in **heart disease** and **nervous troubles**, etc.

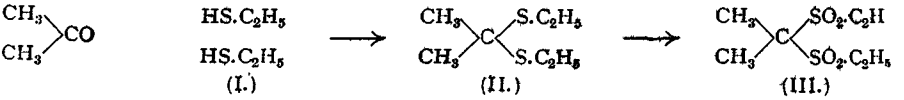
Isopral is **trichlorisopropyl alcohol**, $CCl_3.CH(OH).CH_3$, prepared by treating chloral with methyl magnesium iodide and decomposing with dilute acid—

$$CCl_3.CHO + CH_3.Mg.I = CCl_3.CH.(OMgI).CH_3 + H_2O = CCl_3.CH(OH).CH_3 + Mg(OH)I.$$

Colourless crystals, M.P. 49° C., soluble in alcohol, ether; sparingly soluble in H_2O. Twice as powerful hypnotic as chloral hydrate. Dose, 0.5 to 1 g. In insanity, 2-3 g.

Acetone Chloroform, Chloretone, $(CH_3)_2.C.(OH).CCl_3$, is used as a soporific, inhalation anæsthetic, and a remedy for sea-sickness.

Sulphonal, diethylsulphonedimethylmethane (III.), is prepared by condensing acetone with ethyl mercaptan (I.) and oxidising the resulting compound (II.) with potassium permanganate.



Acetone. Ethyl mercaptan. (I.) (II.) (III.) Sulphonal.

Heavy, colourless prismatic crystals, M.P. 125.5°, soluble in 500 parts of water, 133 parts of ether, and 65 parts of alcohol at 15° C., and in 15 parts of boiling water. It should be free from odour. Used as a sleep producer (dose, 10-20 gr. = 0.65-1.3 g.), also prescribed in epilepsy and in diminishing the sweats of phthisis.

Single, occasional doses do not affect the health, but the continued administration of the drug has been known to lead to serious consequences, such as mental confusion, difficulty of speech and breathing, paralysis of the legs, and finally death.

Trional and **Tetronal** are two drugs closely allied to sulphonal. Their constitution is shown below:—

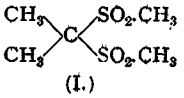
(I.) Trional. (II.) Tetronal.

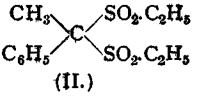
The methods employed in their manufacture are analogous to those employed for sulphonal.

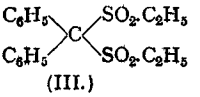
Trional forms colourless crystals, M.P. 76°, readily soluble in alcohol and ether, slightly so in water. The dose for insomnia is from 1-2 g., as an anhydrotic from 0.25-0.5 g. It is contra-indicated in certain affections of the heart.

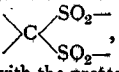
Tetronal forms lustrous leaflets melting at 85° and possessing the solubilities and general action of the last two drugs. Dose, the same as for trional.

The physiological action of these drugs depends on the presence of the ethyl groups, since dimethylsulphonedimethylmethane (I.) is practically without hypnotic effect. Moreover, the intensity of the physiological action increases as we pass from sulphonal to tetronal, *i.e.*, as the number of ethyl groups increases. In this connection it is interesting to note that if one of the methyl groups in sulphonal be replaced by a phenyl group, the resulting substance (II.) is devoid of soporific effect, but if both methyl groups are so replaced an intensely poisonous compound (III.) is obtained.


(I.)

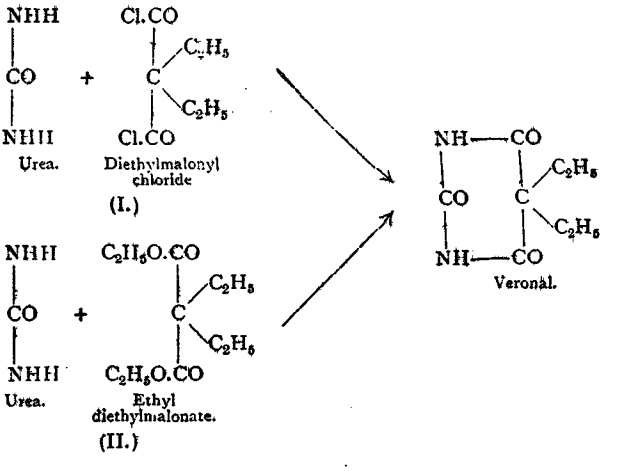

(II.)


(III.)

Keane,* in a lecture delivered before the Liverpool Section of the Society of Chemical Industry, draws attention to the fact that the ethyl groups of the sulphone hypnotics are the agents whereby the grouping  , which is really the carrier of the soporific action, can be brought into combination with the protoplasm of the living organism.

Hedonal, methylpropylcarbinolurethane, $NH_2.CO.O.CH(CH_3)(C_3H_7)$, is prepared by acting on secondary amyl alcohol, $(CH_3)(C_3H_7).CHOH$, with ethyl chlorocarbonate, and then treating with NH_3. Crystals; M.P. 76°; sparingly soluble in cold, easily in hot H_2O. Hypnotic in cases of hysteria or neurasthenia. Dose, 1.5-2 g. in alcohol.

Veronal,† diethylmalonylurea, or diethylbarbituric acid, $C_8H_{12}O_3N_2$, introduced into therapeutics in 1903 by Emil Fischer and von Mering, is prepared by the condensation of diethylmalonyl chloride (I.) or ethyl diethylmalonate (II.) and urea:—



Small transparent crystals; M.P. 191°; soluble in 145 parts H_2O at 20° C., 12 parts H_2O at 100° C. The monosodium derivative is more soluble, and so is frequently employed. An excellent soporific (dose, 0.5-1 g.), superior to most synthetic soporifics in that it is free from unpleasant bye-effects. No injurious effects on the heart. Used in sea-sickness, vomiting, etc.

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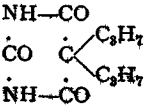
* *Journ. Soc. Chem. Ind.*, 15th April 1910.

† See Merck's "Annual Reports," 1903-1910, and a pamphlet entitled "Veronal" also published by the same firm.

It is very much to be preferred to other drugs in cases where the patient may have to receive a hypnotic for a protracted period, since there seems to be no evidence to show that it produces a habit, although in time the effective dose of the drug may have to be raised slightly. In such cases the treatment may advantageously be varied by the prescription of proponal (see below). It has been successfully used as a partial substitute for morphine in the early stages of treatment of patients striving to break off a habit for that drug.

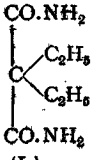
Proponal* is dipropylmalonylurea or dipropylbarbituric acid:—



The preparation is analogous to that of veronal. It is less soluble than the latter drug, dissolving in 70 parts boiling and 1,640 parts cold water. Dose in simple insomnia = 0.15-0.2 g.

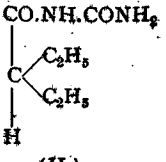
It not infrequently produces a remarkably prolonged effect, a feeling of drowsiness persisting for some hours after awakening. This drug seems to be quite equal to veronal in its freedom from unpleasant effects.

It is probably the presence of the urea residue which is responsible for the soporific effect in veronal and proponal. This is evident from the fact that while the amide of diethylmalonic acid (I.) has no hypnotic effect, diethylacetyl urea (II.)—in which a urea residue has been introduced—is as strong a hypnotic as sulphonal. The action of the urea radical is greatest when it is present in the form of a cyclic ureide, as in the veronal group of hypnotics (III.).



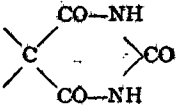
(I.)

Amide of diethylmalonic acid. No hypnotic properties.



(II.)

Diethylacetyl urea. Hypnotic properties.



(III.)

Hypnotic group in veronal and proponal. Strong hypnotic properties.

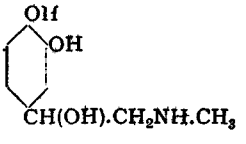
Overton† has shown for a large number of hypnotics that the intensity of the narcotic action of a given drug is proportional to the ratio between its solubilities in oil and in water (*i.e.*, distribution coefficient).

The discovery is important because the material of nerve cells is largely composed of oily or fatty substances (lipoids).

The narcotic drug, after introduction into the system, rapidly finds its way into the blood, in which condition it is practically in aqueous solution; the extent of its narcotic action, or, in other words, the extent to which it permeates the nerve cells, depends, therefore, on the ratio between its solubility in the serum and in the cell lipoids. This applies, of course, to drugs such as chloroform and ether as well as to sulphonal, trional, etc.

ADRENALINE

Adrenaline (epinephrine, suprarenine, hemisine), the active principle of the suprarenal capsules, has the constitution—



Adrenaline forms white, light crystals, M.P. 210°-212°, very sparingly soluble in water, alcohol, and ether; soluble in dilute acids. The aqueous solution has a

* Merck's "Reports," 1905-1909.

† "Studien über Narcose," Dissertation, Jena, 1901; see also Pfluger's *Archives*, 92, 115-280.

bitter taste and is faintly alkaline. In alkaline and neutral solution it is a strong reducing agent, absorbing oxygen from the air and turning brown, the change being accompanied by a diminution in physiological activity.

Adrenaline is known in all three possible forms, viz., laevo-rotatory (*l*), dextro-rotatory (*d*), and racemic (*dl*).

In the suprarenal capsules only the laevo-rotatory base occurs, and this is by far the most physiologically active, being (as regards rise of blood pressure) twelve to fifteen times stronger than the *d*-modification, and *twice* as strong as the *dl* or racemic variety.

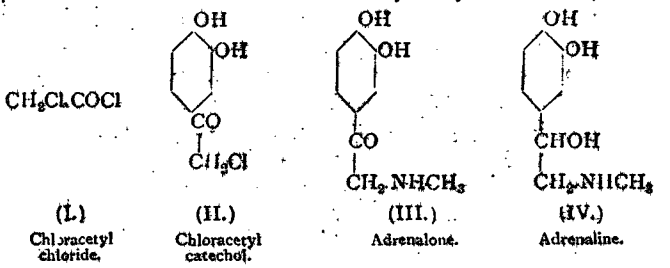
(*a*) **Extraction of *l*-Adrenaline from the Suprarenal Glands.**—Takamine extracted at 95° C. the disintegrated suprarenal glands of sheep or oxen with water acidulated with HCl or acetic acid, concentrated the extract, added alcohol until no further precipitate was thrown down, filtered, evaporated *in vacuo*, and rendered alkaline with ammonia. In a few hours adrenaline crystallised out and was purified by solution in acid and reprecipitation with ammonia. 112 kg. of fresh tissue yield 125 g. adrenaline. $[\alpha]_D = -51.4°$ in HCl.

(*b*) **Synthetic Preparation of Adrenaline** (Stolz).—Chloroacetylchloride (I.) or a mixture of monochloroacetic acid and phosphorus oxychloride is made to react with catechol whereby chloroacetylcatechol * (II.) is produced. This is then mixed with alcohol, and an aqueous solution of methylamine run into the cooled mixture.

The methylamine salt of the chloroacetylcatechol is first produced, but on standing changes to methylaminoacetylcatechol (III.) which crystallises out. This ketone is known as adrenalone; its salts with acids differ from those of adrenaline in that sodium acetate precipitates from them the free base.

By reduction of a solution of adrenalone sulphate by means of aluminium turnings † in presence of mercuric sulphate, adrenaline (IV.) is obtained.

Dakin ‡ has also reduced adrenalone electrolytically.



(I.) Chloracetyl chloride. (II.) Chloracetyl catechol. (III.) Adrenalone. (IV.) Adrenaline.

This preparation of synthetic adrenaline was carried out by *Stolz* whilst working in the laboratories of Messrs Meister, Lucius, & Brüning.

The product is known as synthetic or racemic adrenaline, and is about half as physiologically active as the natural *l*-rotatory adrenaline. The resolution of this racemic adrenaline into *l*-adrenaline—identical in all respects with the natural product—and *d*-adrenaline, has been achieved by Flächer (also of Meister, Lucius, & Brüning's staff) as follows:—

Resolution of Synthetic Racemic Adrenaline.§—Synthetic adrenaline is dissolved in a hot methyl alcohol solution of the molecular equivalent of *d*-tartaric acid, the alcohol removed *in vacuo* at 35°-40°, and the residue crystallised by seeding with the acid *d*-tartrate of *l*-adrenalin. The crystals of the acid *d*-tartrate of *dl*-adrenaline are then stirred with methyl alcohol, when the acid *d*-tartrate of the *l*-base remains undissolved while the isomeric salt passes into solution. The crystals are filtered off, washed, and recrystallised from alcohol until a product is obtained melting at 149°. The **laevo-adrenaline** recovered from this showed a rotation of $[\alpha]_D - 51.4°$ in dilute hydrochloric acid solution, melted at 211°-212° (the melting point of *dl*-adrenaline), and was identical in all respects with the natural *l*-adrenaline obtained from the suprarenal glands.

The dextro-adrenaline is obtained by regenerating the base from the methyl alcohol mother liquors, and submitting it to a similar treatment with *l*-tartaric acid, M.P. 211°-212°; $[\alpha]_D = +51.9°$ in dil. HCl. Very little physiological action.

* *Bull. Soc. Chim.* [3], 12, 1911 (1894).
† *Cent. Blatt.*, 1905 (I.), 315.
‡ *Ibid.* (II.), 57.
§ Flächer, Hoppe-Seyler's *Zeitschrift*, Vol. 58, part 3, p. 189.

Clinical Uses of *l*-Adrenaline.—When injected subcutaneously it intensely contracts the arteries and increases the blood pressure.

So enormously powerful physiologically is adrenaline that the injection of one-millionth of a gram for every 2 lbs. weight of an animal causes the blood pressure to suspend a column of water 7 in. higher than it would otherwise do. A dose of one-twentieth of a milligram intravenously injected in rabbits doubles the general arterial blood pressure, and less than one-millionth of a gram gives a distinct action.

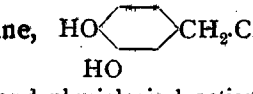
The contractile effect on the arteries is so great that it drives blood away from the injected tissues and thus allows "bloodless" surgery, adrenaline being to-day the most valued styptic known.

It has been used in ophthalmic surgery in conjunction with cocaine or similar drugs (see Section I., p. 603) for the production of local anæsthesia along with anæmia of the conjunctiva. If administered along with an anæsthetic such as chloroform or ether, adrenaline tends to prevent the fatal collapse which sometimes occurs under these conditions, while for minor operations, as in dentistry, when employed along with cocaine, it prevents severe bleeding.

It is employed in the earlier stages of Addison's disease, which arises from a diseased condition of the suprarenal glands. It is also used in cases of catarrh. Strength of solution used for injection is 0.1-0.01 per cent., maximum dose for injection = 0.0005 g.

The introduction of adrenaline into Surgery is largely due to the scientific work of the firm Meister, Lucius, & Brüning.

A number of important recent researches have been made on the connection between the physiological action of adrenaline and its chemical constitution, with the object of ultimately synthesising other drugs with similar or more powerful characteristics. See Dakin, *Proc. Roy. Soc. Lond.*, 76, Series B, 498-503; also *Cent. Bl.*, 1905, ii. 1458, and *Journ. Physiol.*, 1905, 32, p. 35; Loewi and Hans Meyer, *Cent. Blatt.*, 1905, 1111; Barger and Dale, *Journ. Physiol.*, 1910, 41, 19.

3:4-Dihydroxyphenylethylmethylamine, 

is closely allied to adrenaline both in formula and physiological action. It is prepared by the degradation of papaverine (compare Pyman, *Trans. Chem. Soc.*, 1910, 97, 264), and is placed on the market by Burroughs Wellcome & Co. under the name "**Epinine.**"

ERGOT, ETC.

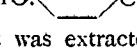
Ergot (*Claviceps purpurea*, *Sclerotium clavus*, and *Spermaldia clavus*), a dark-coloured fungus which attacks damp rye and other grasses, and when contained in flour causes the disease known as **Ergotism**, is much used in midwifery for causing powerful contractile action of the pregnant uterus. When injected, it produces a rise in blood pressure, and is sometimes used to check hæmorrhage from the lungs and other internal organs.

Formerly no method of testing the efficiency of the various ergot preparations was known, but now the strength is ascertained by noting the quantity required to blacken (cause gangrene) a cock's comb.

Ergot is detected in flour by extracting with boiling alcohol, acidifying with H_2SO_4, and examining the alcoholic extract spectroscopically. If ergot is present the solution is reddish and shows characteristic absorption bands.

Chemical Constituents of Ergot.—Ergot is a complex mixture of alkaloids. The chief physiologically active ones isolated are:—

* **Ergotoxine,** $C_{35}H_{41}O_6N_5$, white amorphous powder, is the physiologically active principle of ergot, since it produces a strong rise in blood pressure, causes gangrene of the cock's comb, and powerfully contracts the pregnant uterus, although having little effect on the isolated non-pregnant uterus.

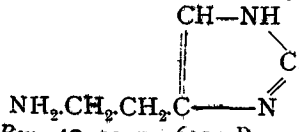
***p*-Hydroxyphenylethylamine,** HO.  $CH_2.CH_2.NH_2$, is present in the aqueous extract of ergot, from which it was extracted and later on synthesised by

* Barger and Carr, *Trans.*, 1907, 91, 347; Barger and Ewins, *ibid.*, 1910, 97, 284.

Barger (*Proc. Physiol. Soc.*, 1909, **37**, 77; *Biochem. Journ.*, 1907, ii. 240; *Trans. Chem. Soc.*, 1909, **95**, 1123, 1720). M.P. 161°. Is now placed on the market by Messrs Burroughs Wellcome & Co. under the name **Tyramine**. In addition to raising the blood pressure and producing strong contraction of the pregnant uterus, it greatly increases the vigour of the heart's action, and may be administered in case of shock or collapse.

Iso-amylamine, $(CH_3)_2CH.CH_2.CH_2.NH_2$, isolated by Barger (*loc. cit.*) from aqueous extract of ergot by steam distillation. Increases the blood pressure and contracts pregnant uterus.

Both *p*-hydroxyphenylethylamine and isoamylamine are present in putrid meat.

4 (or 5)-β-Aminoethylglyoxaline, also known as β-iminazolylethylamine, is also contained in ergot. (Barger and Dale, *Trans.*, 1910, **97**, 2592; Ewins and Pyman, *Trans.*, 1911, **99**, 339; Ackermann, *Zeitsch. Physiol. Chem.*, **65**, 1910, 504). It has the constitution  , and is prepared synthetically (Windaus and Vogt, *Ber.*, **40**, 1907, 3691; Pyman, *Trans.*, 1911, **99**, 668). It is now placed on the market by Burroughs Welcome & Co. under the name "**Ergamine**." It decreases the blood pressure and powerfully contracts the isolated uterus even in a non-pregnant condition.

Hordenine, $HO.C_6H_4.CH_2.CH_2.N(CH_3)_2$, was isolated by Leger* from barley-malt germs, in which it is present to 0.2-0.5 per cent., by extracting with alcohol in the presence of tartaric acid, filtering, neutralising, extracting with ether, and crystallising the product from alcohol. It is a strong base, sparingly soluble in water, soluble in alcohol, ether, $CHCl_3$, etc., and forms crystalline salts with acids. Hordenine retards coagulation of the blood and when injected raises the blood pressure, although not to the same extent as adrenaline or the ergot bases. Not very toxic. Used in dysentery and as a heart tonic. Preparations are placed on the market by Merck and by Burroughs Wellcome & Co. It has been synthesised by Barger (*Trans. Chem. Soc.*, 1909, **95**, 2193).

SYNTHETIC DRUGS USED IN PARASITIC DISEASES, SUCH AS SLEEPING SICKNESS, SYPHILIS, ETC.

Atoxyl, Arsamin, or Soamin, the mono-sodium salt of *p*-aminophenylarsonic acid, $NH_2.C_6H_4.As\begin{matrix}=O\\OH\\ONa\end{matrix}$, is prepared by heating arsenic acid with aniline at 190°-200° C., converting into the sodium salt by agitating with Na_2CO_3, and recrystallising from water.

A white powder, tasteless and odourless, easily soluble in H_2O. Decomposes in stomach and so is given subcutaneously. Used in the treatment of sleeping sickness and syphilis. Dose, about 0.5 g. Incautious treatment may lead to blindness and symptoms of poisoning, (headache, colic). Also used in tuberculosis.

Acetylatoxyl or Arsacetin, $CH_3CO.NH.C_6H_4.As\begin{matrix}=O\\OH\\ONa\end{matrix}$, is soluble in water (1 part in 10). More chemically stable and less toxic than atoxyl. It has been successfully employed in sleeping sickness, skin diseases, and syphilis. Dose, 0.6 g. injected in 10-15 per cent. solution.

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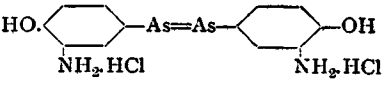
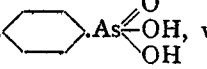
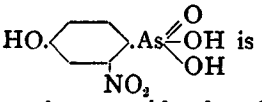
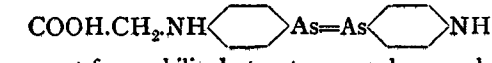
* *Compt. rend.*, 1906, **142**, 108, 143, 234, 916 *et seq.*

Salvarsan, "606," is dihydroxydiaminoarsenobenzene dihydrochloride, and is believed to have the constitution :—



It is prepared, according to the English Patent 13,485, 1910, by nitrating the Na-salt of *p*-hydroxyphenylarsonic acid,  , whereby the nitro-body  is produced; this on reducing with Na-amalgam or Na_2S, condenses, with the ultimate production of the dihydroxydiamino-compound, whose hydrochloride is known as **Salvarsan.** Salvarsan is a bright yellow powder supplied in glass tubes filled with an inert gas to prevent oxidation.

The introduction of **Salvarsan** by Ehrlich and Hata in 1910-1911 caused a sensation in the medical world. It is stated to be a specific cure for syphilis, a single injection into the buttocks having effected a complete cure in many cases. It is placed on the market by Meister, Lucius, & Brüning. See "Salvarsan," by Martendale and Westcott (London, 1911); also Ehrlich and Hata's treatise, "Die Experimentelle Chemotherapie," Berlin, 1911.

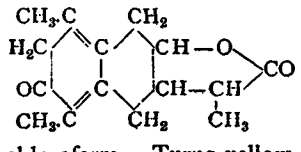
Arsenophenylglycine ("418"), a predecessor of salvarsan, has the formula  . Also a powerful curative agent for syphilis, but not so popular as salvarsan.

Ichthyol is a volatile oil containing sulphur obtained by heating "stink-stone" or "oil-stone"—a bituminous schist found in the Tyrol (Seefeld). The salts of ichthyol sulphonic acid (obtained by treating ichthyol with concentrated H_2SO_4) are used therapeutically, the ammonium salt, **ammonium "sulphoichthyolicum,'** being obtained by neutralising the sulphonic acid with ammonia and evaporating to a syrup. It is sometimes called "ichthyol." It forms a reddish brown syrup, soluble in water, with a smoky taste and smell. Much used externally in cases of skin diseases and internally in cases of tuberculosis, catarrh of the lungs, chronic diseases of the stomach and intestines. The Na-, Li-, and Zn salts are also used.

Ichthyol-Albumen (= Ichthalbine) is obtained by precipitating albumen solution with a solution of ichthyol sulphonic acid. Grey-brown powder, soluble in water, insoluble in the stomach. It decomposes in the intestine into ichthyol and albumen, and is used for intestinal catarrh.

Ichthoform is a compound of ichthyol sulphonic acid and formaldehyde. Dark powder, insoluble, almost odourless and tasteless. Used externally as an **iodoform substitute** for wounds, and internally as an intestinal antiseptic.

Santonine, $C_{15}H_{18}O_3$, the lactone of santoninic acid, $C_{15}H_{20}O_4$, is separated from the blossoms of wormseed and used for destroying intestinal worms. Dose, 0.025-0.05 g. twice daily for children. Maximum dose, 0.1-0.3 g. per diem. Colourless, odourless crystals, M.P. 170°. Sparingly soluble in cold water, more soluble in hot, readily soluble in alcohol, ether, chloroform. Turns yellow in light.



For Trade Names to other new Drugs, see Martin's "Industrial Chemistry," Vol. I., Appendix II., p. 667.

VEGETABLE ALKALOIDS

Alkaloids of Opium.—Opium is a very complex mixture containing along with protein matter and various acids, carbohydrates, gums, waxes, etc., numerous alkaloids of which the most important are: Morphine, about 9 per cent., Narcotine 5 per cent., Papaverine, 0.8 per cent., Thebaine, 0.4 per cent., Codeine, 0.3 per cent., Narceine, 0.2 per cent.

Morphine, $C_{17}H_{19}NO_3$, the most important, is extracted as follows: The aqueous extract of opium is concentrated, and alkaloids precipitated with sodium carbonate. The precipitate is extracted first with water, and then with cold alcohol when most of the morphine remains behind. This is dried, dissolved in dilute acetic acid (any narcotine is insoluble), filtered through animal charcoal and precipitated with ammonia. Purified through its salts or by crystallising from boiling alcohol. Dose of morphine hydrochloride, $\frac{1}{8}$-$\frac{1}{2}$ **grain**.

Atropine, $C_{17}H_{23}NO_3$, occurs in the deadly nightshade (*Atropa belladonna*) and in *Datura stramonium*. It forms heavy needles of M.P. 115°, and is intensely poisonous, and strongly dilates the pupil of the eye, for which purpose a 0.5 per cent. solution is used in ophthalmology. Maximum dose = .001 g.; maximum per day, 0.003 g.

It is also used as a narcotic, and in the night sweats of phthisis. Its constitution is given under **Cocaine** (section on **Local Anæsthetics**).

Strychnine, $C_{21}H_{22}N_2O_2$, occurs along with brucine, $C_{23}H_{26}N_2O_4$, in the seeds of *Strychnos nux vomica*.

Extraction.—The crushed, water-sodden nuts are ground to a pulp, and extracted with hot alcohol, the latter evaporated, the extract treated with lead acetate, and excess of lead removed by H_2S or H_2SO_4. The strychnine is then precipitated with caustic soda, the more soluble brucine remaining almost completely behind.

Colourless crystals, intensely poisonous, a typical spinal poison. Dose, $\frac{1}{30}$-$\frac{1}{12}$ of a grain. It is a valuable tonic, and is employed in paralysis, and in cases of lead poisoning.

Quinine, $C_{20}H_{24}N_2O_2$, is obtained from various kinds of cinchona bark, in which it occurs along with other alkaloids such as quinidine, cinchonine cinchonidine, etc.

Extraction.—The powdered bark is mixed with lime and extracted with high boiling petroleum, the solution being then shaken with dilute sulphuric acid and neutralised *while hot* with Na_2CO_3. The most of the quinine then separates as sulphate, which is further purified by precipitating as insoluble tartrate with Rochelle salt solution.

A white crystalline powder almost insoluble in water, sparingly soluble in cold alcohol, the aqueous solution of its sulphate fluoresces blue. Perhaps the most important drug known, its annual production amounting to 485,900 kg.

Pilocarpine, $C_{11}H_{16}N_2O_2$, occurring in Jaborandi leaves, is the physiologica antithesis of atropine. It is a thick liquid and is used as a sudorific and to check salivation.

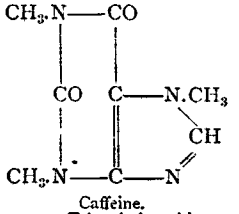
For the chemistry of pilocarpine see papers by Jowett, *Trans.*, 1901-1905.

Hydrastine, $C_{21}H_{21}NO_6$, found in the root of a North American plant *Hydrastis canadensis*, is employed similarly to ergot.

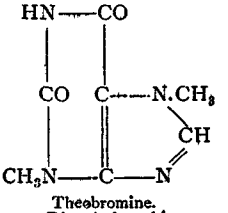
Veratrine.—The commercial product, obtained from the seeds of *Veratrum sabadilla*, is a mixture of various alkaloids. It is a white powder causing violent sneezing and general irritation of the mucous membrane when inhaled.

Yohimbine is an alkaloid obtained from the Yumbehoa tree (Africa). It is employed internally in cases of impotence.

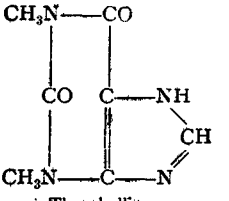
Purine Alkaloids.—Three important drugs belonging to the purine compounds are Caffeine, $C_8H_{10}O_2N_4 + H_2O$, Theobromine, $C_7H_8O_2N_4$, and Theophylline or Theocine, $C_7H_8O_2N_4$.



Caffeine.
1:3:7-Trimethylxanthine.



Theobromine.
3:7-Dimethylxanthine.



Theophylline.
1:3-Dimethylxanthine.

Caffeine occurs in tea and coffee, about 1.4 per cent. in tea. From the waste dust of tea it is extracted by boiling with water, precipitating tannin with lead acetate, removing excess of the latter with H_2S, filtering, and concentrating, when caffeine crystallises out. It is also obtained as a bye-product in the manufacture of caffein-free coffee. Unroasted coffee beans are treated with superheated steam and extracted with benzene, whereby much of their caffein is removed. It is now prepared on the large scale from guano by Böhringen & Sons, of Mannheim.

Caffeine forms white silky needles which lose water at 100°, sublime at 180°, and melt at 230.5°. It is soluble in 80 parts of water at 15° and in 2 parts of boiling water, but is sparingly soluble in many organic solvents such as cold alcohol. Chloroform readily dissolves it.

Used in headache and neuralgia alone or combined with phenacetin, and as a heart tonic. Dose, 0.5 g.; maximum daily dose, 1.5 g. It is employed internally and subcutaneously.

Theobromine, a colourless, odourless, crystalline powder, sublimes at 290°, neither melting nor decomposing. It occurs in cocoa. Combined with a molecular proportion of sodium salicylate, its sodium salt is employed under the name of Diuretin. This is a white powder, soluble in water, and employed in dropsy and in diseases of the kidneys and heart. Theobromine has been synthesised by Traube (*Berichte d. deutschen Chemischen Gesellschaft*, **33**, 1371 and 3035) starting from cyanoacetic acid and methylurea.

Theophylline or Theocine is a stronger diuretic than theobromine. It occurs to a small extent in tea leaves. Sodium theophylline acetate is a valuable diuretic.

Synthetic Preparation.—See D.R. Pat., 151,133, 144,761, 148,208, 138,444 Theophylline itself forms colourless crystals, M.P. 208°. It is difficultly soluble in water, hence the use of soluble double compounds.

The writer desires to thank the following firms for much information regarding the newer synthetic drugs:—Messrs Burroughs Wellcome & Co., London; Messrs Meister, Lucius, & Brüning, Höchst; Messrs Merck, Darmstadt; Messrs Evans, Sons, Lescher, & Webb, Liverpool.

SECTION XXII

The Modern Explosives Industry

THE MODERN EXPLOSIVES INDUSTRY

By William Barbour, M.A., B.Sc.

LITERATURE

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MODERN EXPLOSIVES

Gunpowders

The term "modern," as applied to explosives, is generally understood to connote an explosive other than black gunpowder or the later brown powder. Gunpowder, already known in the middle of the thirteenth century, is still used, however, for sporting purposes and for mining, though it has been discarded by military authorities in favour of the more powerful agents now at our disposal. Its constituents, saltpetre, sulphur, and charcoal, are still mixed in the same way and in the same proportions as formerly (75 per cent. KNO_3, 10 per cent. S, 15 per cent. C).

In this country, **Bobbinite**, essentially a black powder with diminished sulphur content, headed the list of "permitted" explosives arranged in order of quantities used during 1909. A Departmental Committee appointed in 1906 by the Home Office to investigate allegations as to danger arising from the use of Bobbinite in fiery mines, reported that its use should not for the present be restricted. It is made in two varieties: (*a*) KNO_3, 62-65 parts; wood charcoal, 17-19.5 parts; sulphur, 1.5-2.5 parts; together with 13 to 17 parts of a mixture of ammonium sulphate and copper sulphate; or (*b*) KNO_3, 63-65 parts; wood charcoal, 18.5-20.5 parts; sulphur, 1.5-2.5 parts; rice or maize starch, 7-9 parts, and 2.5-3.5 parts of paraffin wax.

H.M. Inspector's report shows that during 1909 out of 30,091,887 lbs. of explosives used in mines and quarries, 17,595,475 lbs. were gunpowder. This constituted 58.5 per cent. of the whole. Gunpowder is not a "permitted" explosive, and in Germany, also, its use in coal mines is forbidden, the prohibition being extended to all powders of the same type.

The great developments of the potash industry in Germany have involved a revival of mixtures resembling black powder, and these have a large sale. Both in that country and in America nitrate of soda, on account of its cheapness, is substituted for potassium nitrate, and charcoal is frequently replaced by brown coal or pitch. **Sprengsalpeter**, for instance, consists of 75 per cent. $NaNO_3$, 15 per cent. brown coal, and 10 per cent. sulphur. Owing to the hygroscopic nature of the sodium nitrate, the mixture of this substance with the carbonaceous material and sulphur is heated to the melting point of sulphur and then pressed, the resulting product being only slightly affected by moisture. Explosives of this type come into commerce either in the form of grains packed in cartridges or as compressed cylinders with an axial canal, and are fired in the same way as black powder. They burn slowly when ignited and fissure the rock rather than shatter it. **Petroklastite** is an explosive of this class and contains: $NaNO_3$, 69 per cent.; KNO_3, 5 per cent.; S, 19 per cent.; pitch, 15 per cent.; $K_2Cr_2O_7$, 1 per cent. The introduction of ammonium nitrate secures a lower temperature during explosion. **Wetter-Dynammon**, made by the Austrian Government for use in fiery mines, contains: NH_4NO_3, 93.83 per cent.; KNO_3, 1.98 per cent.; charcoal, 3.77 per cent.; moisture, 0 42 per cent.; and **Amidé powder** has the composition: KNO_3, 40 parts: NH_4NO_3, 38 parts; charcoal, 22 parts.

Gunpowder, again, is still used in priming compositions in order to initiate the decomposition of high explosives, and in certain types of safety fuse it continues to hold its own. The latter may be compared to a piece of cord having a fine train of gunpowder down the centre. Stress of commercial competition has resulted in the production of a greatly improved fuze which burns uniformly through a definite length in a given time. Attempts to substitute a core of smokeless powder for gunpowder have not as yet yielded a satisfactory result.

Chili saltpetre (sodium nitrate) contains perchlorates, as also does "conversion" saltpetre or potassium nitrate prepared from it. To this circumstance, when discovered, was attributed the origin of various disastrous explosions which had previously occurred, but later work has shown that, in ordinary cases, the danger arising from the presence of a small percentage of the more sensitive perchlorate has been over-estimated (Dupré, *Journ. Soc. Chem. Ind.*, 1902, 825; Lunge and Pergmann's paper read at Fifth International Congress of Applied Chemistry, Berlin, 1903). Bergmann recommends a maximum of 0.4 per cent. of perchlorate for blasting powders and 0.2 per cent. for gunpowders.

Nitro-glycerine, the trinitric ester of glycerol, $C_3H_5(ONO_2)_3$, is an important constituent of a great many explosives used as propellants or for blasting. Should the price of glycerol continue at its present high figure it is not improbable that explosives made from cheaper raw materials will displace it to some extent.

The process of manufacture now about to be described is the outcome of a long series of improvements which have been made at intervals upon the methods originally adopted by Alfred Nobel, the pioneer in the commercial production of this substance. The nitrator-separator in its present form was first used at Waltham Abbey in the Royal Gunpowder Factory, and is the subject of the British Patent 15,983 of 1901, taken out by Colonel Sir Frederic L. Nathan, R.A., Mr J. M. Thomson, F.I.C., and Mr Wm. Rintoul, F.I.C.

The apparatus is shown diagrammatically in the accompanying figure in both plan and elevation. The nitrating vessel *a* has the form, generally used, of a lead cylinder with sloping bottom and conical lead roof. The mixed acids are not introduced from above, as has been customary, but through a pipe connected with the lowest part of the bottom. This pipe has three branches, *b*, *c*, and *d*; *b* leads to the denitrating plant, *c* to the drowning tank, while *d* ascends and divides into two branches of which one is connected with the storage tank for mixed acid and the other to the waste acid tank. The acid pipe bend is one foot lower than the lowest part of the bottom so that, during stirring, no nitro-glycerine may enter the ascending pipe. On the sloping bottom of the vessel lies a coil *g* provided with several holes for the introduction of compressed air for stirring, and in the cylindrical portion of the vessel are cooling coils *h h* of lead pipe through which water, refrigerated if necessary till its temperature is below 10° C., flows. The conical roof is surmounted by a lead cylinder *e* with two windows *f* and side outlet, which is connected with the lead pipe *k* down which the nitro-glycerine flows to the pre-wash tank. From the pipe *k* ascends another pipe *m*, through which fumes are aspirated. *s* is a thermometer, the bulb of which dips into the mixture inside *a*.

To carry out a nitration, the mixed acids, consisting of 41 per cent. HNO_3, 57.5 per cent. H_2SO_4, and 1.5 per cent. H_2O in the ratio of 6.09 of mixed acid to 1 of glycerine, are allowed to enter through *d*, air-stirring is begun, and the glycerine is introduced by means of an injector, the mixture being cooled by the coils *h h*. The glycerine, owing to its viscosity at ordinary temperatures, must have been

previously warmed to 30°-35° C., and its rate of admission is regulated so as to prevent the temperature from rising above 22° C. When nitration is finished, and the temperature has fallen a little, the air in *g* and the water in *h* are shut off, and the mixture then begins to separate.

The temperature should not have been allowed to fall below 15° C. Waste acid from a previous operation is now allowed to enter the apparatus slowly from beneath, through *d*, and forms a layer of gradually increasing depth below the reaction mixture which thus rises slowly in the vessel. The nitro-glycerine reaches the cylinder *e*, and runs off through *k* to the pre-wash tank, containing water, and is subjected to an alkaline washing. The displacing acid enters at such a rate as to cause clear nitro-glycerine, free from suspended acid, to flow through the outlet as separation proceeds. Finally a sharp line of demarcation between acid and nitro-glycerine is observed through *f*, and the inflow of acid through *d* is stopped. The contents are allowed to stand for a time in order to obtain the best possible yield of nitro-glycerine.

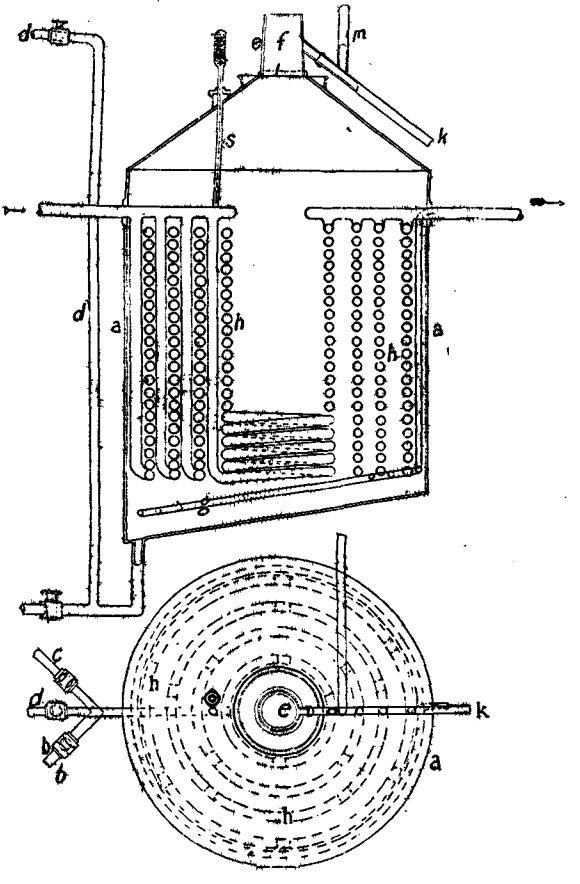

FIG. 238.—Nathan, Thomson, and Rintoul's Nitrator-Separator.

Under the old régime the waste acid was run off to a special building, the after-separating house, in which nitro-glycerine still remaining in the acid separated out slowly during the course of several days. This was skimmed off from time to time, and put into a vessel filled with water in which it was washed. A workman was required to be in attendance day and night. The modern practice is to destroy the nitro-glycerine in the waste acids immediately after nitration by the following method, due to Sir F. L. Nathan and Messrs Thomson and Rintoul:—

Sufficient waste acid is run off from the nitrator-separator to avoid splashing over during stirring, which is again started by turning on the compressed air. Water amounting to 2 per cent. of the waste acid is slowly added, and mixes immediately with the acid through the stirring. The temperature rises slowly during the addition of the water, about 3° C. for each per cent. of water added, and air stirring is continued after the addition of water till the temperature begins to sink. The air is then shut off, and waste acid again run in from beneath till the surface reaches the upper outlet. On standing for a time nitro-glycerine adhering to the sides of the vessel and the cooling coils may ascend, and can be run off through *k*. The waste acid, now completely free from nitro-glycerine, is allowed to run off through *b*, as much as will be necessary for displacement of nitro-glycerine in a later operation being elevated to the storage tank communicating with *d*, while the remainder is run into a tank where it stays without further supervision until it is denitrated.

Owing to the introduction of this process the nitro-glycerine never passes through an earthenware cock at any stage of its manufacture and a source of danger is thereby removed. A further lessening of risk is achieved by the removal of the nitro-glycerine immediately after its separation from the acid, by the cooling during separation and after separation, by decrease in amount of manipulation of nitro-glycerine and waste acid, and by the disappearance of the necessity for an after-separation

building. The saving in differences of level necessary to transport the nitro-glycerine from building to building is very considerable, and the area necessary for the factory is now less than formerly. A plant consisting of two nitrating vessels and one pre-wash tank nitrates five charges each of 1,450 lbs. of glycerine daily.

After removal of acid from the nitro-glycerine in the pre-wash tank, accomplished by air-stirring with water and finally with an alkaline solution, the nitro-glycerine is allowed to run through a rubber pipe attached to the lowest point of the sloping bottom of the pre-wash tank into the gutter, which has a fall of 1 in 60 and leads to the final washing house. During the preliminary washing the rubber pipe is secured to a nozzle fixed to the outside of the tank at a point above the level of the liquid.

In the final washing house the nitro-glycerine is subjected to prolonged treatment with alkaline solution, using air-stirring as before. The alkali remaining after this treatment is removed by washing with pure warm water, and the nitro-glycerine is afterwards filtered by passing it through a mat of sponges in order to free it from small quantities of flocculent impurities and suspended mineral matter. A diagram of the plant is shown in the figure (Fig. 239.)

By the use of the acid mixture above mentioned, obtained from 2.8 parts of nitric acid and 3.4 parts of fuming sulphuric acid (20 per cent. SO_3), Sir F. L. Nathan and Mr Wm. Rintoul have,

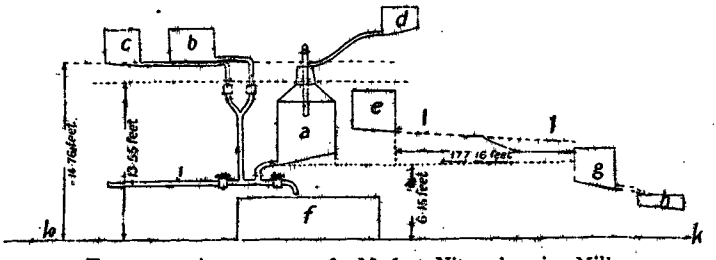

FIG. 239.—Arrangement of a Modern Nitro-glycerine Mill.

A. The Nitrator-Separator
B. The Mixed Acid Tank
C. Waste Acid, for Displacement Tank
D. Glycerine Tank
E. Pre-wash Tank
F. Drowning Tank
G. Final Washing Tank
H. Filter
I. Pipe for running off waste Acid.
K, K. Ground Level
L, L. Gutter, with fall of 1 in 120

using the above process, increased the yield of nitro-glycerine to 230 parts per 100 parts of glycerine (British Patent, 6,581, 1906). By former processes in which 100 parts of glycerine were added to a mixture of 300 parts of 94 per cent. HNO_3 and 500 parts of 96 per cent. H_2SO_4, the yields varied from 210-215 per cent. Using this acid mixture in the Nathan, Thomson, and Rintoul process the yield was increased to 220 per cent., the theoretical yield being 246.7 per cent.

The use of waste acid from a previous nitration which is brought to its original composition by the addition of fresh acid gives, according to data from the Zentral-stelle, Neu Babelsberg, yields of 228 per cent. (British Patent, 2,776, 1905). Details regarding the influence of mixed acids which have been thus revivified upon the time necessary for complete purification of the nitro-glycerine are not available.

The process of separation, after nitration, is frequently protracted owing to the action of gelatinous silicic acid in preventing the nitro-glycerine from passing from the emulsified form to that of a separate layer of pure liquid. In order to obtain a quick and well-defined separation the Dynamit A. G. (D.R. Patent, 171,106, 1904) at Hamburg, add, during nitration, paraffin or fatty acids of high molecular weight in proportions of 0.5-2 per cent. by weight of the glycerine, while Reese (U.S.A. Patent, 804,817, 1905) uses .002 per cent. of sodium fluoride, whereby the silicic acid is converted into silicon tetrafluoride.

After-separation has been shortened, on the laboratory scale, by Escales and Novak (British Patent, 18,597, 1907) by the use of the electric current, but is entirely obviated in the Nathan,

Thomson, and Rintoul process. Evers (D.R. Patent, 182,216) has described a new process for denitrating waste acid, in which a mixture of air and steam at a high temperature enters the denitrating tower at one or more points.

Properties of Nitro-glycerine.—Kast has found that nitro-glycerine has two solidification or melting points (*Zeitschr. Schiess-Sprengstoffwesen*, i. 225). The lower melting phase is a labile product and changes completely into the stable higher melting modification on stirring with a crystal of the latter, which melts at about 13° C. The thawing of frozen nitro-glycerine has been a fruitful source of accident, and attention has been directed towards obtaining a product which will remain liquid under the conditions to which it is subjected during cold weather. The well-known effect of adding soluble ingredients is to produce a **depression of freezing point** proportional to the amount dissolved, and nitro-benzene and ortho-nitrotoluene were used for this purpose. Other nitric esters of glycerine, however, which do not appreciably diminish the explosive power of the product to which they are added, have recently found extended use for this purpose.

Dinitro-glycerine (glycerine dinitrate), first prepared by Mikolajzak in 1903 for use in depressing the freezing point of trinitro-glycerine (British Patent, 27,706, 1904), may be prepared alone, and then added to the latter, or, more conveniently, the two esters may be generated simultaneously under suitable conditions in the proportions required.

One method of working (Heise, "Der Bergbau," 1907, Heft 35) is to nitrate the glycerine in nitric acid, allowing the temperature to rise to a certain extent; the solution of the ester in nitric acid is then allowed to stand for about two hours, and separation of the ester is then effected by diluting with water and neutralising with carbonate of lime. After separation, the dinitro-glycerine still contains water and acid, the latter being removed by adding soda and the water by a special process. A reddish yellow oil of sp. gr. 1.5 is thus obtained. The calcium nitrate solution obtained as a bye-product is treated with ammonium sulphate; the ammonium nitrate formed is used in explosives manufacture, and the sulphate of lime as a manure. Extraction of the diluted acid mixture, both before and after neutralisation, by means of ether, has been tried on the small scale, and Escales and Novak have proposed glycerine disulphuric ester as the starting point for the preparation. The method of preparing a mixture of di- and trinitro-glycerine is described by Mikolajzak (*loc. cit.*).

The technical product is a mixture of two isomeric modifications. Its purification is difficult.

According to Will (*Berichte*, 1908, 1107; *Zeitschr. Schiess-Sprengstoffwesen*, 1908, 324) the dinitrate, in the water-free condition, is not solid at ordinary winter temperatures, but offers little advantage over nitro-glycerine from the point of view of sensitiveness to shock. It is hygroscopic, and when moist is less sensitive, but at the same time loses its faculty for forming no solid on subjection to winter temperatures.

Nitrate of Polymerised Glycerine.—By appropriate heat treatment 2 molecules of glycerine condense to form 1 molecule of diglycerine with splitting off of water. By treating the diglycerine so formed with mixed nitrating acids, tetra-nitro-diglycerine, $\begin{matrix} C_3H_5(ONO_2)_2 \\ C_3H_5(ONO_2)_2 \end{matrix}\!\!>\!O$, is obtained, which behaves like trinitro-glycerine as regards solubility in organic solvents, insolubility in water, and ease of detonation with fulminate of mercury. The addition of 20-25 per cent. of the product to trinitro-glycerine will prevent it from freezing at ordinary winter temperatures.

Will and Stöhrer (*Zeitschr. Schiess-Sprengstoffwesen*, i. 231) polymerised glycerine by heating it for seven or eight hours to 290°-295° C., and obtained a product containing 60 per cent. diglycerine and 4-6 per cent. of tri- or polyglycerines. These were separated by fractional distillation under reduced pressure. By repeated treatment pure diglycerine can be obtained as a clear, viscous, sweet liquid, soluble in water, having a sp. gr. of 1.33, and distilling undecomposed at 240°-250° C. under 8 mm. pressure.

Escales and Novak treat glycerine with hydrochloric acid and nitrate the resulting mixture of monochlorhydrin, dichlorhydrin, diglycerine, chlorhydrin of diglycerine, triglycerine and chlorhydrin of triglycerine (*Deutsche patentanmeldung*, 12th May 1906).

Claessen (British Patent, 9,572, 1908) produces diglycerine and polyglycerines in a much shorter time than usual by heating the glycerine with a small quantity of alkali (0.5 per cent.) to 275°-280° C. The glycerine, diglycerine, and polyglycerine can be separated by fractional distillation.

Dinitromonochlorhydrin.—By passing hydrochloric acid gas into glycerine heated to 70°-100° C., a mixture of α- and β-monochlorhydrins is obtained

[$CH_2Cl.CH(OH).CH_2(OH)$] and [$CH_2(OH).CHCl.CH_2(OH)$]. These are separated from the reaction mixture by fractional distillation under reduced pressure, and are afterwards nitrated alone or in admixture with glycerine. In the latter case the reaction is claimed to be less dangerous, and the separation quicker (Welter, British Patent, 6,361, 1905). Dinitromonochlorhydrin is easily stabilised in the usual way, and stands the Abel heat test for a much longer time than ordinary nitro-glycerine. It is a pale yellow liquid with a faint aromatic smell, soluble in ether, alcohol, acetone, chloroform, etc., and insoluble in water and acids. Its sp. gr. is 1.5408 at 15° C., and it boils at atmospheric pressure at 190°-193° C. If boiled under a pressure of 15 mm., no partial decomposition takes place, and it distils over at 120°-123° C. as a colourless oil.

It is surprisingly insensitive to shock and friction, is not hygroscopic, does not freeze at − 25° to − 30° C., and dissolves easily in nitro-glycerine. The addition of 20 per cent. to nitro-glycerine renders it practically unfreezable. It is said to be an excellent gelatinising medium for nitro-cellulose. One disadvantage it possesses, viz., the formation of HCl on explosion, but this can be rectified in large measure by adding an alkali nitrate to the explosive.

Di-nitro-acetin and Di-nitro-formin are produced by the nitration of mono-acetin, $C_3H_5(OH)_2.O.CO.CH_3$, and monoformin, $C_3H_5(OH)_2.O.CO.H$. Their properties resemble those of dinitromonochlorhydrin, and they have been used for making unfreezable nitro-glycerine explosives (see *Zeitschr. Sch.-Sprengstoffwesen*, 21, 1907). (See p. 383.)

Gun-cotton

The process now coming into general use for gun-cotton manufacture is the result of important improvements devised by Messrs J. M. and W. T. Thomson of the Royal Gunpowder Factory, Waltham Abbey (British Patent, 8,278, 1903; D.R. Patent, 172,499, 1904). The following description is taken largely from the paper by Colonel Sir F. L. Nathan in the *Journal of the Society of Chemical Industry*, 27th February 1909. To the Council of the Society and to Sir Frederic Nathan my best thanks are due for their kind permission to use the accompanying illustrations.

The raw materials are cotton waste and sulphuric and nitric acids. Ordinary cotton waste varies considerably in character, and this is not without effect on the character of the resulting gun-cotton. Before it is received at the works it has been subjected to treatment with alkaline, bleaching and acid liquors in succession, after which it has been washed and dried; or the oil, etc., has been extracted with benzol. The physical condition of the cotton, and, to some extent, its chemical properties, are affected by this process, and an undue proportion of "fly" or finely divided and felted material will hinder the penetration of mixed acids during nitration and diffusion of waste acid from the sphere of reaction, and may indicate the presence of products of hydrolysis or of oxidation of cellulose. Oxy-cellulose exerts an influence on the nitrogen content of the gun-cotton and on its solubility in ether alcohol if it be present in appreciable quantity. Hydrocellulose, produced by hydrolytic action, yields a nitro-cellulose agreeing in properties with that obtained from untreated cellulose so far as nitrogen content and solubility in ether alcohol are concerned. The viscosities of nitro-hydrocellulose solutions in acetone are less than those of similar nitro-cellulose solutions, however, and this fact taken in conjunction with the power of reducing Fehling's solution and of fixing methylene blue, possessed by hydrocellulose, indicates a structural change which may possibly affect adversely the stability of gun-cotton containing its esters.

Blotting-paper made from cotton, paper shreds, tissue paper, cellulose as used for paper making, and other raw materials have been suggested for the manufacture, but all have been discarded, and even celluloid and artificial silk makers use cotton, though paper is still largely used in the manufacture of celluloid.

The prepared cotton waste on arrival at the factory contains a notable percentage of hygroscopic moisture, also wood, pieces of iron, metal, string, rubber, etc. The mechanical impurities are removed as far as possible by hand-picking, and the cotton is then passed through a teasing machine (Fig. 240), which separates the cotton fibres and opens out knots and lumps. It is then again picked over as it leaves the machine.

At Waltham Abbey the cotton, as it leaves the teasing machine, is delivered on to an endless band which carries it to the drying machine. The moisture is expelled from the cotton by a blast of hot air supplied by a fan through a steam heater. The cotton waste passes very slowly through

the machine, the operation lasting about three-quarters of an hour, and issues from it containing about ½ per cent. of moisture. It is immediately weighed out into charges and placed in sheet-iron boxes or other suitable receptacles, with lids, to cool, for which a period of about eight or nine hours is sufficient. During the cooling the cotton waste reabsorbs about half a per cent. of moisture.

The nitric and sulphuric acids employed are commercial products of a fairly high standard of purity. The waste acids are revivified to a larger extent than formerly, by the use of Nordhausen sulphuric acid and concentrated nitric acid, and are used again for nitration.

The nitrating apparatus consists of a number of units of four pans worked together, Figs. 241 and 242. The pans are of earthenware and circular, 3 ft. 6 in. in diameter and 10 in. deep at the side of the pan; the pan has a fall of 2 in. to the outlet, which is ¾ in. in diameter, and is supported on earthenware pedestals about 1 ft. 10 in. above the floor level. The four members of each unit are connected together by lead pipes, and these again are connected to the nitrating acid supply pipe, to the strong and weak waste acid pipes, and to a waste water pipe, through a gauge-box where the rate of flow is determined whilst the waste acids are being run off.

The process proceeds as follows: A small perforated plate is placed over the outlet of each pan, and four perforated segment plates making a complete disc of diameter about 1 in. less than that

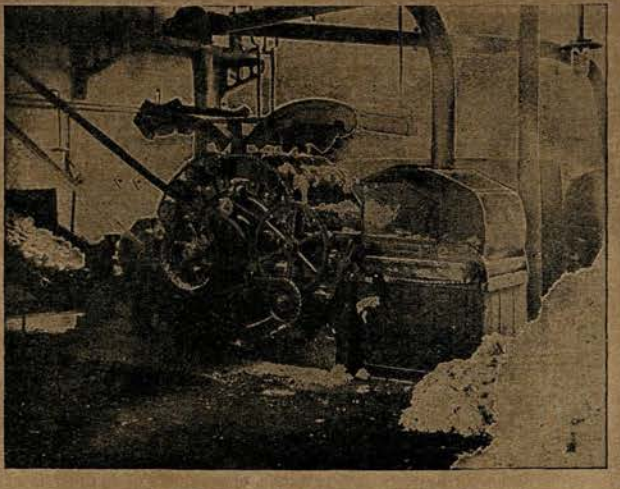

FIG. 240.—The Teasing Machine.

of the pan are placed on the bottom. Aluminium fume hoods, which are connected to an exhaust fan, having been placed on the four pans, nitrating acid, which is cooled in summer and warmed in winter, is allowed to rise to the proper level in the pans. There are then 600 lbs. of mixed acids above the bottom plates and 50 lbs. below. A charge of 20 lbs. of cotton waste is then immersed in the acid, handful by handful, aluminium dipping forks being used for the purpose. When all the cotton waste has been pushed under the surface of the acid, perforated plates, in segments, are placed on the top of it, care being taken that all cotton waste is below the surface of the acid, and a film of water, at a temperature of 5°-8° C., is run very gradually on to the surface of the plates through a distributor. The film of water prevents the escape of acid fumes and the fume hoods are then removed. The time required for dipping a charge is a quarter of an hour. Nitration is allowed to proceed for two and a half hours. The cock leading to the gauge-box is then opened and waste acid is run off at the rate of about 17 lbs. a minute. Water, cooled if necessary, is run on to the top of the perforated plates, through the distributor, at an equivalent rate. The major portion, amounting to about 80 per cent. of the total waste acid, is returned to the acid store tanks to be revivified with Nordhausen sulphuric and new nitric acids. The remaining 20 per cent. of the waste acid is sent to the acid concentration factory for denitration and concentration. The quantity of acid thus dealt with amounts to about 4 lbs. for every pound of gun-cotton.

	H_2SO_4.	HNO_3.	HNO_2.	H_2O.
Composition of waste acid to be revivified (=80 per cent. of total waste acid) - - - -	72.70	17.30	0.65	9.35
Composition of waste acid to be denitrated and concentrated (=20 per cent. of total waste acid) -	61.0	17.35	0.55	21.10

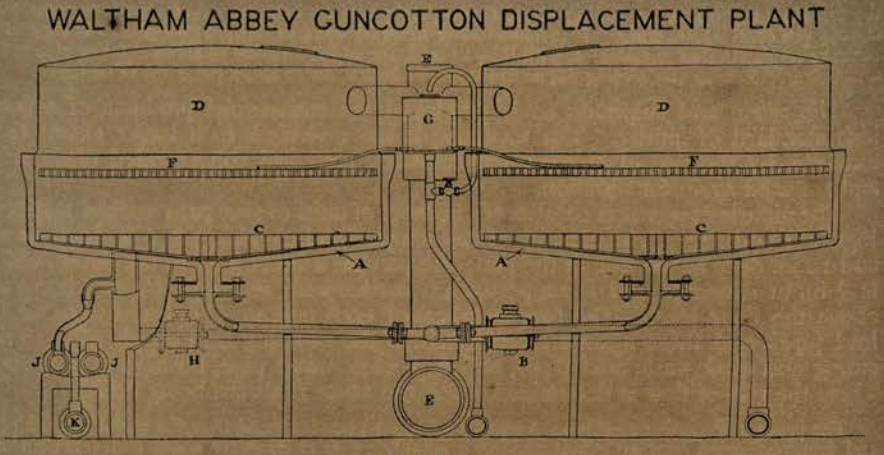

FIG. 241.

A small proportion of the water which follows the recoverable waste acid is slightly acid to the extent of 0.1 lb. for every pound of gun-cotton made, and this represents the total loss of acid (=0.4 per cent.). Mr G. W. MacDonald (*Journ. Soc. Chem. Ind.*, 20th February 1911) finds that the sulphuric acid is displaced at a relatively more rapid rate than the nitric acid.

Stabilisation or thorough purification of the gun-cotton next follows. Adsorbed acids should not be neutralised at an early stage of the purification process, as their hydrolytic action upon various impurities is an important factor at this juncture.

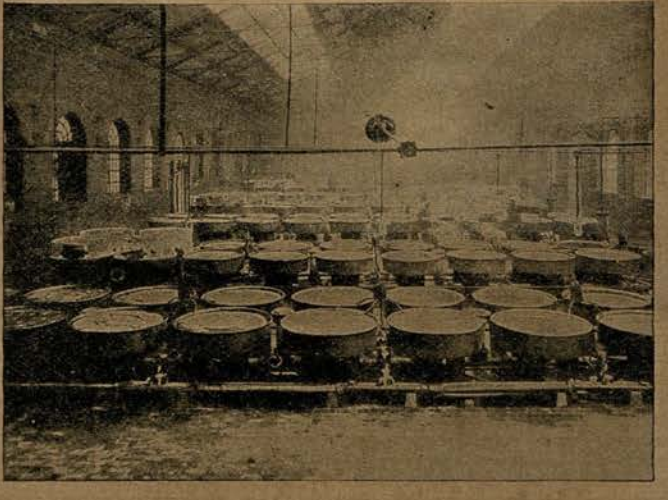

FIG. 242.—Gun-cotton Nitrating House, Waltham Abbey.

Amongst the impurities to be removed are mixed sulphuric and nitric esters, nitrous esters, nitric esters of sugars, and substances produced by the action of the mixed acids on seed husks and on the dried juices in the tubular cotton fibres. These are eliminated or rendered harmless by prolonged boiling of the gun-cotton in large wooden vats (Fig. 243), the water being changed at intervals.

Dr Robertson (*Journ. Soc. Chem. Ind.*, 16th July 1906) has shown the advantage of acidity in the earlier boilings for promoting rapid hydrolysis of the mixed sulphuric and nitric esters.

Treatment with alkaline solutions is not so efficient and may produce hydrolysis of the gun-cotton itself to a considerable extent. The method of boiling in use at Waltham Abbey for periods of 12+12+4+4+4+4+4+2+2+2 hours, with a cold water washing between the first and second and second and third boilings, produces a stable gun-cotton. The nature of the water supply affects the period necessary for stabilisation, and a system in which the gun-cotton is wrung in centrifugals between the boilings, or one in which the pulped gun-cotton is subjected to boiling water treatment, will shorten the time necessary for complete purification. Boiling in closed vessels under pressure has been tried with good results.

The following table is taken from Sir Frederic Nathan's paper :—

Process.	Nature of Dipping Vessel.	Acids.					Cotton Waste Used, lbs.	Acid Used per lb. Cotton Waste.	Time of Nitration. Hours.	Yield on Dry Cotton Waste per Cent	Output per Man per Week.
		Analysis per Cent.				Quantity, lbs.					
		H_2SO_4.	HNO_3.	HNO_2.	H_2O.						
Abel - -	Cast-iron pan and earthenware pot	74.00	18.00	0.60	7.40	13.75	1¼	11.0	12	163.75	458
Ardeer—direct dipping	Cast-iron pot	75.00	15.75	1.30	7.95	127	4½	28.2	12	159.00	1,112
Dartford—nitrating centrifugal	Centrifugal machine	69.35	23.15	...	7.50	800 to 1,100	16 to 24	50.0	1	160.00	...
Waltham Abbey—displacement	Earthenware pan	70.50	21.00	0.60	7.90	650	20	32.5	2½	170	1,742

The gun-cotton is then pulped in a beating engine similar to those used for pulping the raw material in paper manufacture (see Figs. 244, 74). The fibres are thus materially shortened and crushed, and impurities retained in the fibres are removed mechanically or by diffusion. The gun-cotton pulp is then freed from particles of metal, grit, and foreign bodies by running it, suspended in a large volume of water, along a shallow trough having grit traps placed in it at intervals. These retain the heavier gritty particles, and fine sand is retained by a strip of blanket which is laid along the bottom of the trough.

At Waltham Abbey the pulp is next washed in a vessel termed a "poacher" (Figs. 244, 74). These hold each about 10 cwt. of gun-cotton and 1,100 gals. of water, and are fitted with power-driven

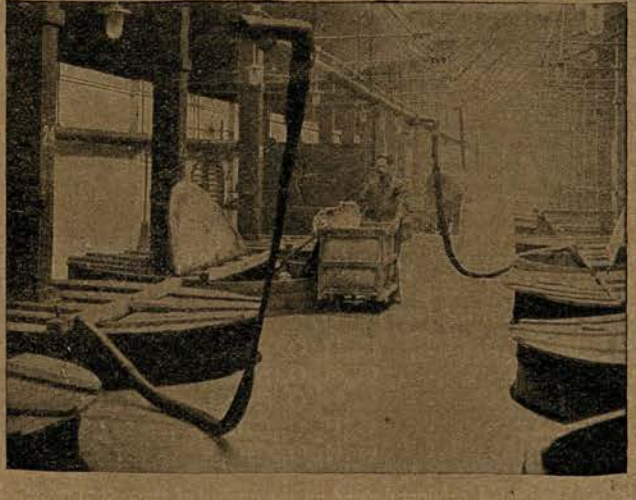

FIG. 243.—The Boiling House.

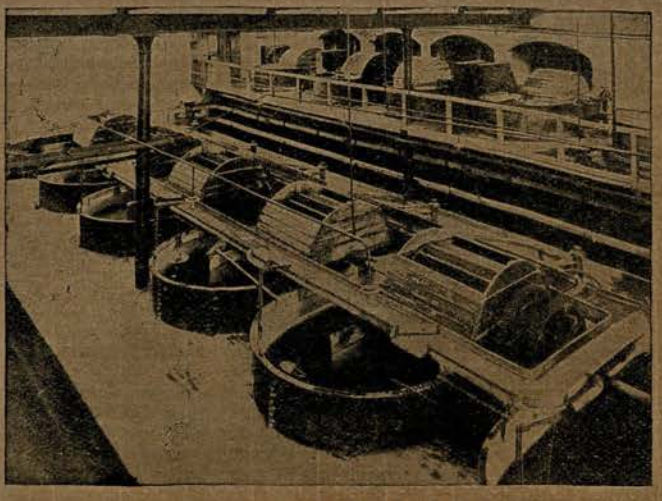

FIG. 244.—"Beaters" and "Poachers." (See p. 198.)

paddles for agitation purposes. The gun-cotton receives at least three washings, and is allowed to settle down after each washing, the washing water being removed by a skimmer. Poaching serves as an opportunity for effecting the final stage of a system of blending which is carried on throughout the manufacture.

The pulp is then moulded by light hydraulic presses into cylinders 5½ in. high and 3 in. in diameter, which enables it to be dried on fixed racks in the drying house without having recourse to movable drying trays or similar arrangements. Less dust is produced than when the gun-cotton is dried in the form of ordinary pulp.

If intended for use in mines, torpedoes, or other demolition work, the gun-cotton is moulded into suitable shapes, and the moulds are then subjected to powerful hydraulic pressure, amounting to about 6 tons per square inch, to produce the finished slabs or primers.

Brown showed that a large quantity of wet gun-cotton can be detonated by interposing between a detonator and the moist gun-cotton a primer of dry gun-cotton (British Patent, 3,115, 1868). Recently a primer of trinitro-toluene has been proposed (D.R. Patent, 200,293, 1906). The pressing of large masses of gun-cotton which are then turned in a lathe to shapes required has been successfully carried out in recent years (Hollings, British Patent, 8,278, 1903).

Claessen (D.R. Patent, 200,262, 1906) proposes to displace the nitrating acids retained in nitro-cellulose by sulphuric acid and the latter by water. Comte de Briailles (D.R. Patent, 203,377, 1906) sends an electric current through the acid mixture during nitration in order to keep the nitrating acid at suitable concentration and temperature. Sir F. L. Nathan, J. M. Thomson, and W. T. Thomson (British Patent, 7,269, 1903) remove the water from wet nitro-cellulose by displacement with alcohol. The Salpetersaure-Ind.-Ges. (D.R. Patent, 180,587, 1906) revivify the waste acid after nitration by electrolysis, using the waste acid as anode liquid, and dilute nitric acid in the kathode compartment.

Assuming the cellulose unit to be $(C_6H_{10}O_5)_4$ or $C_{24}H_{40}O_{20}$, many nitric esters of cellulose are capable of being synthesised, but those met with in practice are comprised among the following (see p. 207):—

Dodecanitro-cellulose	$C_{24}H_{28}O_8(NO_3)_{12}$	with	14.14	per cent. nitrogen.
Endecanitro-cellulose	$C_{24}H_{29}O_9(NO_3)_{11}$	,,	13.47	,, ,,
Decanitro-cellulose	$C_{24}H_{30}O_{10}(NO_3)_{10}$	,,	12.75	,, ,,
Euncanitro-cellulose	$C_{24}H_{31}O_{11}(NO_3)_9$	,,	11.96	,, ,,
Octonitro-cellulose	$C_{24}H_{32}O_{12}(NO_3)_8$	,,	11.11	,, ,,

The properties of the nitrated product depend on the quality of the cotton waste, the proportion of mixed acid to cotton the moisture content of the atmosphere, the ratio of H_2SO_4 to HNO_3, the

water content of the acid mixture, and on the time, temperature, and method of nitration. Many years ago (1901) Mr W. T. Thomson of Waltham Abbey prepared a specimen of nitro-cellulose having a nitrogen content of 13.94 per cent., obtained by drowning the nitrated product in alcohol, but under ordinary working conditions the gun-cotton contains 12.8-13.10 per cent. of nitrogen. The solubility of the product in ether alcohol, formerly thought to be simply a function of the nitrogen content, is influenced by the method of nitration. Collodion cotton, containing 11-12 per cent. nitrogen, is soluble in ether alcohol. According to Lunge (*Zeitschr. Angew. Chem.*, 2,051, 1906), nitro-cellulose soluble in ether alcohol is obtained by nitrating dry cotton in a mixture of equal parts HNO_3 and H_2SO_4 together with 17-18 per cent. of water, *i.e.*, 41 per cent. H_2SO_4, 41 per cent. HNO_3, 18 per cent. H_2O. Guttmann (*Zeitschr. Angew. Chem.*, 1907, 262) gives an example from practice in which equal parts of nitric acid of 75 per cent. monohydrate and sulphuric acid of 96 per cent. monohydrate (also a mixed acid with 14.5 per cent. water) are used in 25 parts of which 1 part of cotton is nitrated for 1-1½ hours at 40° C.

Although by strict adherence to a definite set of conditions during manufacture a product of unvarying properties is obtained, this is never an individual cellulose ester but a mixture of esters in which one or two predominate. Berl (D.R. Patent, 199,885, and *Zeitschr. Sch. Sprengstoffwesen*, 81, 1909) proposes to depolymerise the cellulose molecule by heating the cotton in inert gases. Nitro-celluloses prepared from depolymerised cellulose are claimed to be better than those made from ordinary cotton as regards solubility and capacity for gelatinisation. Collodion cotton finds extended use in the manufacture of gelatinised nitro-glycerine explosives. It is also used in photography and surgery and in large quantities for the manufacture of celluloid and artificial silk. The total world's production of artificial silk is estimated at 5.5 million kilos., of which 2 million kilos. are collodion silk (Massot, *Zeitschr. Angew. Chem.*, 433,444, 1911), see pp. 207, 208, 212.

Of other nitric esters, those from sugar, mannite, and starch are the most important, but various defects have prevented the adoption of the first two to any considerable extent. **Nitro-starch**, on the other hand, is now used quite largely in America for blasting explosives, and its cost of production is said to be considerably less than that of nitro-glycerine. Hough (British Patent, 12,627, 1904) dissolved starch in nitric acid at a temperature of 90° F., and precipitated the nitro-starch by passing gaseous sulphuric anhydride into the solution. In a later patent he altered his process by nitrating the starch with a mixture of 3 parts of nitric acid of 95 per cent. monohydrate and 2 parts of 98 per cent. sulphuric acid, and adding so much sulphuric anhydride to it as to furnish a concentration of 100 per cent. with 1 to 2 per cent. of SO_3 in the solution. Further, during nitration he injects more sulphuric acid having an excess of about 2 per cent. anhydride, and claims to obtain in this way an octonitrate having the formula $C_{12}H_{12}(NO_2)_8O_{10}$ and a nitrogen content of 16.5 per cent. The product is said to be quite stable and to be suitable for use as a blasting explosive either alone or when it forms 10 per cent. of a mixture containing sodium nitrate and carbonaceous material. It has been utilised in the manufacture of smokeless powder. Berl and Büttler (*Zeitschr. Sch. Spr.*, 82, 1910) have tested Hough's data and have found them incorrect. The maximum percentage of nitrogen in nitrate of starch was found by them to be 13.44 per cent.

Dynamite, Blasting Gelatine, Gelatine Dynamite, and Gelignite

With the object of rendering nitro-glycerine safe for transport and use, Alfred Nobel devised the mixture with kieselguhr known as dynamite. Nobel's guhr dynamite consisted of 75 per cent. of nitro-glycerine and 25 per cent. of kieselguhr, an earth containing tubular siliceous skeletons of diatoms which performed the function of a physical container or carrier. Various inert substances have been used instead of kieselguhr, *e.g.*, magnesia alba, tripoli, and Boghead coal ashes. Among dynamites with combustible absorbents may be mentioned Reid and Borland's carbo-dynamite in which burnt cork charcoal is used. It contains 90 per cent. of nitro-glycerine and is consequently more powerful than dynamite, the more so as the absorbent is combustible. Another class of dynamite contains absorbents which are themselves explosive, and a further subdivision of this class may be made into those which contain nitro-cellulose and those which do not.

Kieselguhr dynamite formed only 0.4 per cent. of the total amount of explosives used in mines and quarries during 1909 (H.M.I. report).

For its manufacture the guhr is freed from moisture and organic matter by ignition and is then crushed and sifted. A test is made to determine its capacity for absorbing nitro-glycerine, and if it should prove to yield a dry crumbling dynamite which would give unsatisfactory cartridges it is suitably blended with another batch possessing less absorptive capacity or is mixed with a small quantity of barium sulphate (say 1 per cent.). On the other hand the dynamite should not contain excess of nitro-glycerine or the latter will exude.

The guhr, containing less than half a per cent. of moisture, is weighed out in equal quantities into a series of bags or cases which are taken on trucks to the

purified nitro-glycerine store-house where the required amount of nitro-glycerine is accurately measured and added to each batch of kieselguhr. The bags or cases are then removed to the mixing house where their contents are first well mixed by hand and afterwards passed through a sieve. The dynamite is now transferred to the cartridge huts in bags or wooden boxes lined with sheet zinc, and there is made into cartridges of diameter and length required by a "continuous" type cartridge press. The cartridges, wrapped in acid-free parchmentised or paraffin-waxed papers, are collected from the huts at frequent intervals and taken to the packing house, whence samples are despatched to the laboratory for subjection to the heat test and exudation test.

Kieselguhr dynamite is orange-yellow or reddish brown in colour (sometimes ochre is added to the guhr) and is plastic to the same degree as fresh mould. Its specific gravity is 1.5 when it contains 75 per cent. of nitro-glycerine. Small quantities of it burn quietly when ignited but larger quantities soon explode; when saturated with paraffin oil it may be ignited without danger in small quantities at a time. A blow of 0.75 kg.-m. will cause its detonation, and it can be exploded by a strong electric discharge.

Direct contact with water brings about separation of the nitro-glycerine, and this constitutes a source of danger when the explosive is used in wet places. Its liability to freeze is another source of danger. Very strong detonators are required to explode it when frozen, and though in this condition it is fairly insensitive to a blow, breaking or crushing are distinctly dangerous operations. Thawing must be conducted with great care in a specially constructed pan provided with a jacket for hot water. Should exudation of nitro-glycerine take place during thawing this will introduce an element of danger in ramming.

During storage, exposure to the influences of damp and sunlight must be avoided. About 1 per cent. of sodium or calcium carbonate is frequently added to the ordinary ingredients in order to preserve neutrality.

Rhenish dynamite contains 70 per cent. of a solution of 2-3 per cent. of naphthalene in nitro-glycerine, 3 per cent. of chalk, 7 per cent. barium sulphate, and 20 per cent. of kieselguhr. Nobel's Ardeer powder contains 31-34 per cent. nitro-glycerine, 11-14 per cent. kieselguhr, 47-51 per cent. magnesium sulphate, 4-6 per cent. potassium nitrate with ½ per cent. of ammonium or calcium carbonate.

Dynamites with a combustible base include carbo-dynamite and others in which the absorbent is wood-meal or sawdust. These latter may be detonated when wet and can be dried before use without marked alteration.

The following are examples of mixed dynamites containing an explosive base in addition to nitro-glycerine: 40 per cent. nitro-glycerine, 12 per cent. wood-meal, 46 per cent. sodium nitrate, and ½-1 per cent. calcium or magnesium carbonate. In a French ammon-dynamite, ammonium nitrate is used. It has the following composition: 40 per cent. nitro-glycerine, 10 per cent. wood-meal, 10 per cent. sodium nitrate, 40 per cent. ammonium nitrate.

In mixed dynamites the nitro-glycerine is capable of being displaced by water, as in the case of guhr dynamite. This potential cause of accidents is removed by transforming the nitro-glycerine into a component of a colloidal solution, which is effected by dissolving 7-10 per cent. of collodion cotton in 93-90 per cent. of nitro-glycerine whereby **Blasting gelatine**, a tough elastic mass and one of the most powerful blasting explosives, is formed.

A colloidal solution containing 96-97 per cent. of nitro-glycerine and 4-3 per cent. of collodion cotton, on being mixed with saltpetre and wood-meal in a kneading machine, yields Gelatine dynamite, or Gelignite, of which the following is a typical example: 62.5 per cent. nitro-glycerine, 2.5 per cent. collodion cotton, 25.5 per cent. sodium or potassium nitrate, 8.7 per cent. wood-meal, and 0.8 per cent. soda. Another containing ammonium nitrate has the following composition: 50 per cent. nitro-glycerine, 2.5 per cent. collodion cotton, 45 per cent. ammonium nitrate, 2.5 per cent. rye-meal, and is known as ammongelatindynamite.

Gelignite formed 10.2 per cent. of the total quantity of explosives used in mines and quarries in this country during 1909, and blasting gelatine and gelatine dynamite together formed 2 per cent. (H.M.I. report).

For the manufacture of these explosives finely pulped and dried collodion cotton is chosen containing not less than 11 per cent. of nitrogen, and having a maximum solubility in ether alcohol and a minimum of gun-cotton or unnitrated cotton. It

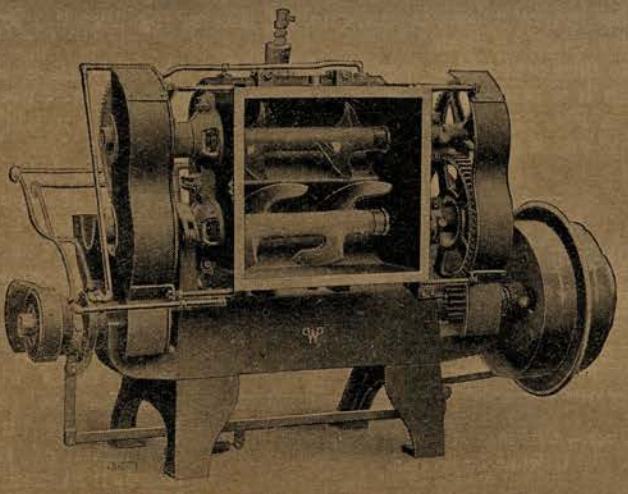

FIG. 245.—Messrs Werner, Pfleiderer, & Perkin's Mixing Machine.

should be free from sand or grit and leave a maximum residue of 0.25 per cent. on ignition. The moisture present should amount to not more than 0.25-0.5 per cent., so exposure to the air is avoided during transit from the drying house to the sifting house. Here the cotton is rubbed gently through a brass sieve, and after being weighed out into air-tight zinc-lined cases or india-rubber bags is removed to the gelatine mixing house where the necessary quantity of pure dry nitro-glycerine is poured upon it in a lead-lined trough. The mixture is well stirred with a wooden paddle and kept for half an hour at a temperature of 40° C. by means of hot-water circulation through the jacket with which the tank is provided. Arrangements should be made for the admission of cold water to the jacket in case the mixture becomes too hot. When the jelly has become semi-transparent it is transferred to the mixing machine, of which an illustration is shown (Fig. 245). M'Roberts' mixing machine is still in use, however (Fig. 246).

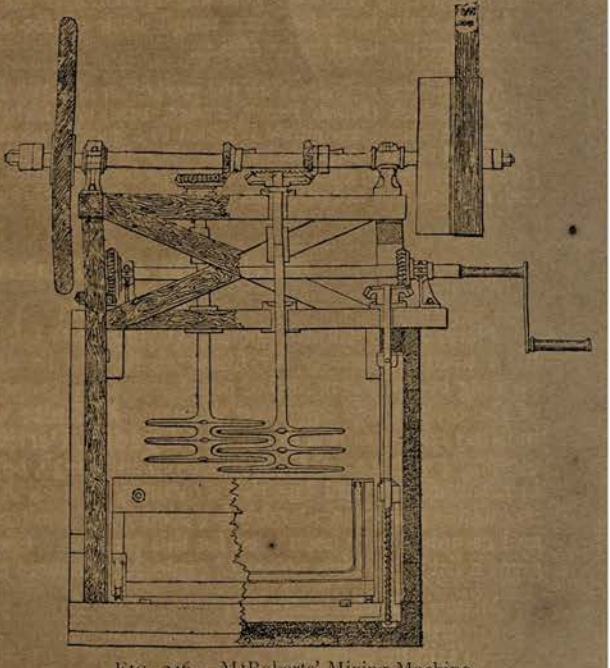

FIG. 246.—M'Roberts' Mixing Machine.

At this point, if gelignite or gelatine dynamite is being made, the necessary proportions of purified wood-meal and potassium nitrate are added, together with a certain amount of one of the substances proposed for depressing the freezing point of nitro-glycerine and a little magnesium carbonate. During mixing the charge is maintained at a temperature of 40° C. by

means of the hot-water jacket surrounding the mixing trough. Incorporation requires at least half an hour.

The paste thus obtained is transferred from the mixing house to the cartridge huts, in which it is made into cartridges by an Archimedean screw machine of the type shown in Fig. 247; the cylinder of paste issuing from a nozzle of required diameter is cut into the lengths appropriate for each size of cartridge.

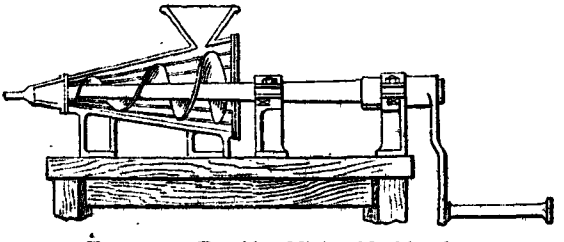

FIG. 247.—Cartridge Mixing Machine for Gelatine Explosives.

Homogeneity, stability, complete absorption of nitro-glycerine, and freedom from tendency to exude are of the highest importance in these explosives.

Blasting gelatine is an amber-coloured, translucent, elastic mass which stiffens somewhat as time elapses. If well made it resists the conditions of the test for exudation and stands the heat test for a longer period than the minimum of ten minutes. It explodes at 204° C. if heated slowly (Hess), and at 240° C. if the heating is rapid. It is also exploded by a blow of 3½ kg.-m. between steel and steel, but is much more sensitive to shock when frozen.

Gelatine dynamite is equally sensitive in its normal soft condition and when frozen, and in both cases is exploded by a weaker blow than is blasting gelatine. The insensitiveness of the latter when it contains camphor is somewhat remarkable. The shattering effect of gelatine dynamite is less than that of blasting gelatine, which is only used for very tough rock or for military purposes, and resembles nitro-glycerine itself in its effects.

Among recent suggestions for the production of gelatinous explosives may be mentioned those of Schachtebeck (British Patent, 22,645, 1902) and Bichel (British Patent, 23,846, 1902). In the former, ammonium nitrate is added to a gelatine consisting of glue or dextrin, glycerine and water, and this is incorporated with a nitro-glycerine gelatine and a carbohydrate. In the latter, glue is dissolved in glycerine, and nitro-glycerine is added. Collodion cotton or a suitable dope such as wood-flour and potassium nitrate may be added before the nitro-glycerine.

Picric Acid and Trinitro-toluene

Picric acid or trinitro-phenol, $\left(C_6H_2\begin{matrix}OH\\(NO_2)_3\end{matrix}\right)$, the oldest organic dye-stuff, has been used extensively for filling shells, and its salts have formed constituents of priming compositions and of powders used as propellants. The honey-yellow colour of the molten acid suggested the name **Melinite** which it receives in France, while in other countries it is designated **Lyddite, Pertite, Ecrasite,** or **Schimose**. Its melting point, 122.5° C., is inconveniently high, so in order to secure greater ease in manipulation and less risk a quantity of a soluble substance sufficient to depress its melting point considerably is added to it. Dinitro-toluene, mononitro-naphthalene, and camphor have been used for this purpose. Girard (British Patent, 6,045, 1905) gives a list of melting points of explosive mixtures of this kind:—

Mixture in Equimolecular Proportions of—	M.P.	M.P. of Mixture
Trinitro-phenol	122° C.	49° C.
Nitro-naphthalene	61° C.	
Trinitro-phenol	122° C.	47° C.
Dinitro-toluene	71° C.	
Trinitro-phenol	122° C.	70° C.
Trinitro-cresol	107° C.	

Mixture in Equimolecular Proportions of—	M.P.	M.P. of Mixture.
Trinitro-phenol	122° C.	78° C.
Trinitro-cresol	107° C.	
Trinitro-phenol	122° C.	80° C.
Trinitro-cresol	107° C.	

The specific gravity of picric acid solidified from fusion is 1.64. A priming composition, such as a mixture of ammonium picrate and potassium nitrate, is necessary to detonate the hard mass.

The manufacture of picric acid is carried out in the following way (*Zeitschr. Schiess. Sprengstoffwesen*, 15, 1909).

Phenol-sulphonic acid is first prepared, $\left(C_6H_4\begin{smallmatrix}OH\\ \diagup\\ \diagdown\\ SO_3H\end{smallmatrix}\right)$, which is then transformed into dinitro-phenol-sulphonic acid $\left(C_6H_2(NO_2)_2\begin{smallmatrix}OH\\ \diagup\\ \diagdown\\ SO_3H\end{smallmatrix}\right)$. The latter decomposes on warming with nitric acid according to the equation :—

$$C_6H_2(NO_2)_2\begin{smallmatrix}OH\\ \diagup\\ \diagdown\\ SO_3H\end{smallmatrix} + HNO_3 = C_6H_2(NO_2)_2(OH) + H_2SO_4.$$

12 parts by weight of phenol are heated to 100°-105° C. for eight hours with 48 parts of sulphuric acid of sp. gr. 1.84, with constant stirring, in a vessel provided with a steam jacket. The melt is drawn off into a transportable earthenware vessel in which, on cooling, it solidifies to a butter-like mass. This is transferred by means of a scoop, in small portions at a time, to 90 parts of nitric acid of sp. gr. 1.385 contained in a large earthenware vessel which stands in a water-bath, stirring being continuous during the whole operation, and the temperature being kept below 20° C. This causes the phenol-sulphonic acids to change into dinitro-phenol-sulphonic acid.

When all the sulphonic acid has been introduced, which for 100 kg. requires about twenty hours, the water surrounding the nitrating vessel is slowly warmed, by leading in steam, so that the temperature rises to 40°-50° C. within the first four hours, and the water is then heated to boiling point. At 80°-90° C., large quantities of nitrous fumes are evolved which are conducted through earthenware pipes to absorption towers; the vigorous reaction having subsided, the water in the heating bath is kept boiling for three to four hours longer, and the contents of the vessel are stirred at intervals with a strong glass or porcelain rod. Heating is then discontinued, and the contents of the vessel are allowed to cool to 30°-35° C, when the picric acid appears almost entirely in the crystalline form. The waste acid is syphoned off, and several water washings are followed by wringing in a centrifugal, which is lined with woollen cloth, and into which cold water is sprayed until the drainings contain traces only of H_2SO_4. After wringing, the picric acid still contains 10-15 per cent. of water, and its further drying is effected by placing it on glass plates in a warm air current or in a vacuum drying apparatus.

The yield from 100 parts of phenol, melting at 40° C., amounts to not more than 190 parts of picric acid, of melting point 121°-122° C., while theory requires 243 parts. The diminution in yield is to be attributed to oxidation due to the excess of nitric acid used. At the same time a considerable excess of nitric acid is necessary in order to avoid the production of lower nitro-derivatives of phenol.

The high melting point of picric acid is not its only disadvantage. It will have been noticed that during manufacture all contact with metals is avoided. Some of the metallic picrates are extraordinarily sensitive to shock, for instance those of lead, iron, and copper, and these salts are formed if the acid comes in contact with the metals or their oxides. Under favourable circumstances their detonation may take place, and, simultaneously with it, that of all the picric acid surrounding them, or in the immediate neighbourhood, hence the necessity for varnishing the interiors of shells, for giving special protection to primers, and for taking the utmost precaution to prevent access of foreign bodies. Picric acid will generate other acids from salts containing their radicles, and will decompose nitric esters, and if used at all it should be used alone. The dust from it is poisonous as also are the fumes arising from the molten acid, and its dyeing effect upon the skin is well known. Ammonium picrate and nitre, the constituents of **Brugère's** powder, are now used as a priming composition.

Trinitro-toluene has sprung into prominence as a substitute for picric acid, chiefly owing to its freedom from acidic properties, its lower melting point and great stability. Of the various isomers the one having the structure

$C_6H_2(NO_2)_3.CH_3.(1_{CH_3}:2:4:6)$ is used. Its manufacture from pure toluene is carried out in stages.

180 kg. of pure toluene are first of all transformed into **mono-nitro-toluene** by means of a mixture of 315 kg. of sulphuric acid (sp. gr. 1.84) and 200 kg. of nitric acid (sp. gr. 1.44); the waste acid is drawn off, and a fresh acid mixture of 600 kg. of sulphuric acid (sp. gr. 1.84) and 200 kg. of nitric acid (sp. gr. 1.48) transforms the first product into dinitro-toluene. The mixture is heated and stirred during the operation, and the dinitro-toluene separates as an oily layer from the hot mixed acids. The waste acid from this second stage is revivified by the addition of 135 kg. of fresh nitric acid (sp. gr. 1.44), and is used again for making mono-nitro-toluene.

Dinitro-toluene forms, on cooling, a pale yellow, fibro-crystalline, moderately hard and brittle mass, which on further treatment with sulphuric and nitric acids is transformed into **trinitro-toluene.** For this purpose it is dissolved by gently heating it with four times its weight of sulphuric acid (95-96 per cent.), and it is then mixed with one and a half times its weight of nitric acid (90-92 per cent.), the mixture being kept cool. Afterwards it is digested at 90°-95° C., with occasional stirring, until the evolution of gas ceases, which takes place in about four or five hours. The product, after cooling, is separated and washed. According to W. Rintoul (*Journ. Soc. Chem. Ind.*, 1915, 34, 61), the M.P. of 1-2-4-6-trinitro-toluene is 80.80°-80.85° C.

According to the purity of the **dinitro-toluene** one may obtain an end-product with a melting point of 72°-73° C., or a purer form with a solidifying point of 77°-79° C. The impure form is used exclusively in blasting explosive mixtures. By recrystallising the higher melting product from alcohol or petroleum benzene it may be obtained pure, and then melts at 80.6° C. It is finely crystalline, is bright yellow in colour, has no specially bitter taste, and the dust arising from it is said to have no injurious effect. Whether in the form of powder, or in the massive condition after pressing or fusion, it is quite insensitive and much safer to manipulate than picric acid. It can be detonated with a No. 3 detonator (0.54 g. of fulminate composition) when in the form of powder, and no poisonous gases are produced. It is quite stable under the influence of heat and moisture, and has no action upon metals or metallic oxides.

Its low density is a drawback (1.54 against 1.64 for picric acid). Rudeloff (*Zeitschr. Schiess. Sprengstoffwesen*, 7, 1907) obtains a density of 1.85 to 1.90 by making a plastic substance from trinitro-toluene and potassium chlorate with a gelatine made from dinitro-toluene and soluble nitro-cellulose. Bichel (British Patent, 16,882, 1906) makes a plastic "compound" with collodion cotton, liquid dinitro-toluene, and larch turpentine to which he gives the name **Plastrotyl.** Messrs Allendorf mix the trinitro-toluene together with some lead nitrate or chlorate with a gelatine made from dinitro-toluene and nitro-cellulose, and call the product **Triplastit.** Bichel (British Patent, 19,215, 1906) melts the trinitro-toluene and, after first exhausting all occluded air, compresses the molten product during cooling by means of compressed air. In this way he increased the density to 1.69. Rudeloff, using hydraulic presses, subjects it to a pressure of 2,000-3,000 atmospheres whereby it attains to a density of 1.7, and can be cut and worked like gun-cotton. For the purpose of facilitating detonation some loose trinitro-toluene is used as a primer.

Trinitro-toluene has been introduced into the French service under the name of **Tolite.** The Spanish Government call it **Trilit.** The carbonite works of Schlebusch are introducing it into other services under the name of **Trotyl,** and Messrs Allendorf of Schoenebeck under the name of **Trinol.**

Trinitro-benzene is also receiving attention as a suitable material for filling shells.

Schroetter and von Freiherr (British Patent, 8,156, 1907) have proposed the use of hexa-nitro-diphenylamine, in a compressed condition, or its salts, in the manufacture of high explosives for adjusting the sensitiveness and the melting point.

Other nitro-derivatives of hydrocarbons and of phenols are used in explosive mixtures. Among the former are dinitro-benzene, chlor-dinitro-benzene, dinitro-toluene, di- or tri-nitro-derivatives of mesitylene, pseudocumene, and xylene, dinitro-naphthalene. Trinitro-naphthalene and tetra-nitro-naphthalene have also been proposed. Of the nitro-phenols, perhaps the most important is tri-nitro-cresol, known as **Cresilite** in France, where it is added to **Melinite.** Other nitro-derivatives of the aromatic series will be mentioned in the section on detonators.

Ammonium Nitrate Explosives, Safety Explosives

Bichel in conjunction with Dr Mettegang and other colleagues has investigated experimentally the conditions which determine the superiority of some explosives over others, with regard to their liability to ignite mixtures of pit gas and air. They have proved that this liability depends upon the length, duration, and temperature

of the flame accompanying detonation, and the figures obtained on dividing the duration of flame by the time of detonation, to which they give the name "**after-flame**" ratio, distinguish in no uncertain fashion those explosives which may be considered "**safe**" from those which are known to be **unsafe**. Even a "safe" explosive becomes dangerous if more than a certain amount of it, known as the "**charge limit**," be used at one time.

In testing explosives for "safety" in this country, a ballistic pendulum is used to ascertain the quantity of explosive equal to 4 oz. of dynamite No. 1, and this quantity, after being stemmed, is fired in air containing 15 per cent. of ordinary lighting gas contained in a long wooden or iron "gallery" of circular or elliptical cross section. If the mixture does not fire in twenty shots the explosive is considered safe. In most other countries the "charge limit," or quantity of the explosive which will just not fire a certain pit gas mixture is determined. In Germany the shots are unstemmed, and the charges fired are heavier than in this country (10½-12 oz.), but a more dilute gas mixture is used (7-9 per cent. methane in air). The less the area of cross section of the gallery the more easily does ignition take place, so until a standard type of gallery is agreed upon, and a definite method of testing is adhered to, the results from the various testing stations can have little value for purposes of comparison. The similar study of the behaviour of mixtures of coal dust and air with various explosives has been carried out on the large scale within recent years, with the result that practical suggestions have been formulated for preventing or arresting the propagation of the explosion wave, while much attention has been paid to the question of the measures best suited for eliminating coal dust, as far as possible, from the air of coal mines.

Gunpowder, trinitro-toluene, picric acid, blasting gelatine, gelatine dynamite, and gun-cotton are all unsafe. Explosives containing nitro-glycerine may, however, be perfectly safe; in fact, such explosives are amongst the safest we have. In these the percentage of nitro-glycerine is comparatively low, and the other ingredients are such as will give as low a temperature as is consistent with satisfactory work. Ammonium nitrate is very frequently used in safety explosives, and a small amount of nitro-glycerine will ensure its complete detonation. Many safety explosives contain ammonium nitrate and compounds of the type of dinitro-benzene, while in others, which contain no ammonium nitrate, the cooling effect of substances like ammonium oxalate or salts containing water of crystallisation is relied upon to confer the necessary degree of safety. While ammonium nitrate explosives in general may be said to have a higher "charge limit" and a less violent shattering effect than the explosives mentioned above, and possess the further advantages of being safer to handle and transport and of requiring a strong detonator, it must not be forgotten that their use is best confined to a definite type of work. The hygroscopic nature of ammonium nitrate is a disadvantage which is overcome by various devices, but its low specific gravity necessitates greater expense in preparing the larger bore-holes necessary to accommodate the charge.

For use in the production of explosives the ammonium nitrate is dried, finely ground, mixed with the other ingredients in a drum-mixer, again dried at 60° C., and afterwards made into cartridges. The cartridges for protection against moisture are either surrounded by tinfoil or impregnated with paraffin or ceresine, which is accomplished by dipping them in a bath containing these substances in the molten condition.

Rigid cartridges are produced by pressing a mixture made plastic either by means of a molten binding material (a nitro-hydrocarbon) or by a solution—collodion cotton in acetone for example. On cooling, or on evaporation of the solvent, the solid cartridge is obtained.

The following are explosives containing ammonium nitrate: Ammoncarbonite, Wetterfulmenite, Chromammonite, Roburite, Dahmenite, Dorfite, Bellite, Securite, Trench's flameless explosive, Faversham powder, Ammonite, Electronite, Amvis, etc.

As mentioned above, the addition of various salts to the explosive mixture for the purpose of reducing the temperature of the detonation products has been made. Claessen (British Patent, 2,240, 1906) uses chrome alum or ammonium chrome alum; the Castroper Sicherheitssprengstoff Akt.-Ges. (British Patent, 18,275, 1905) use ammonium chloride and potassium oxalate; Curtis and others (British Patent, 24,934, 1902) suggest copper sulphate, or a mixture of copper sulphate with ammonium sulphate or equivalent salts. The fire extinguishing compound of Mr Geo. Trench, consisting of sawdust impregnated with a mixture of alum and chlorides of sodium and ammonia, is so disposed about the explosive proper as to prevent the ignition of a surrounding explosive gas

mixture. Nearly all safety explosives require a No. 6 detonator and are generally fired by low tension fuses connected to a magneto firing apparatus. The composition of a few members of this large class is given in the appendix to this article. An apparently practical proposal for supervision of the mine gases is made by Teclu (*J. Prakt. Chem.*, 82, 237-240, 1911, Chem. Lab. der Wiener Handelsakademie) who tests the gas mixtures at various parts of the mine by drawing samples through tinned iron tubes, by means of a powerful suction pump, into explosion vessels situated on the surface. The gas samples can be tested in a few minutes with perfect safety, and the results signalled.

Plasticity is a desirable quality in an explosive intended for use in bore-holes, and ammonium nitrate explosives possessing plasticity are now produced.

Gelatineastralite contains ammonium nitrate with some sodium nitrate, up to 20 per cent. of dinitro-chlorhydrin and maximum amounts of 5 per cent. of nitro-glycerine and 1 per cent. of collodion cotton. **Gelatinewetterastralite** 1 has the composition: 40 per cent. ammonium nitrate, 7.5 per cent. sodium nitrate, 16 per cent. dinitro-chlorhydrin, 4 per cent. nitro-glycerine, 0.5 per cent. collodion cotton, 0.5 per cent. wood-meal, 8 per cent. potato starch, 2 per cent. rape seed oil, 1 per cent. nitro-toluene, 2 per cent. dinitro-toluene, 14 per cent. salt, and 2.5 per cent. ammonium oxalate. Another plastic ammonium nitrate explosive known as **Plastammone** contains ammonium nitrate, glycerine, mono-nitrotoluene, and nitro-semicellulose.

The use of aluminium powder as an ingredient of explosives, first suggested by Dr Richard Escales in 1899, results in a rise of temperature and a considerable increase in pressure produced by the heat evolved during the oxidation of the aluminium, in other words, the explosive power is increased.

The high price of aluminium powder and its liability to oxidise prematurely have militated against its more general adoption. **Ammonal** is an explosive containing aluminium powder, and a similar mixture has been used in Austria-Hungary for several years for filling shells. The latter has approximately the following composition: 47 per cent. ammonium nitrate, 1 per cent. charcoal, 30 per cent. trinitro-toluene, and 22 per cent. aluminium. It is compressed, heated to 67° C., dipped in molten trinitro-toluene, and cooled in a stream of air.

Calcium-silicon, ferro-silicon, silicon, silicon carbide, magnesium, zinc and its alloys, copper, and the rare metals have all been the subjects of patents regarding the production of effects similar to those of aluminium.

Chlorate and Perchlorate Explosives.

The developments of electro-chemistry having resulted in the production of chlorates in large quantity, an outlet for these was sought in the sphere of explosives and ultimately found. Chlorates have long been forbidden for explosives manufacture on account of the sensitiveness of mixtures containing them to shock and friction. Street found, however, that by using castor oil in the mixture this danger was obviated (D.R. Patent 100,522, 1897; 100,532, 1897; 117,051, 1898; 118,102, 1898). **Cheddites**, so-called from their place of manufacture, Chedde, in Haute-Savoie, are composed as follows (Dr Escales' article on "Explosivstoffe," Dammer's "Chemische Technologie der Neuzeit"): (1) $KClO_3$ 79 per cent., nitro-naphthalene 15 per cent., castor oil 6 per cent.; (2) $KClO_3$ 79 per cent., dinitro-toluene 15 per cent., nitro-naphthalene 1 per cent., castor oil 5 per cent; (3) $NaClO_3$ 75 per cent., dinitro-toluene 19 per cent., nitro-naphthalene 1 per cent., castor oil 5 per cent.; (4) $KClO_3$ 80 per cent., dinitro-toluene 2 per cent., nitro-naphthalene 10 per cent., castor oil 8 per cent.

The dinitro-toluene and nitro-naphthalene are dissolved in warm (60°-70°) castor oil contained in a double-walled enamelled iron vessel, and the finely pulverised, dried and sieved potassium chlorate is added with constant stirring or kneading by means of a large wooden paddle. After further working the explosive is corned and on standing for some time is made into cartridges which are waterproofed.

A **cheddite** containing ammonium perchlorate has the following composition: 82 per cent. ammonium perchlorate, 13 per cent. dinitro-toluene, and 5 per cent. castor oil. HCl is evolved in its decomposition, and is not entirely prevented from forming by the addition of sodium nitrate. It possesses, in a high degree, the disadvantage, shared by chlorate cheddites, that it easily becomes hard, and is then not completely detonated.

Colliery steelite consists of 74 parts of potassium chlorate, 25 parts of oxidised resin, and 1 part of castor oil.

Silesia Powder (186,829, 1902, D.R. Patent) is a mixture of 75 per cent. potassium chlorate and pure or nitrated resin. **Permonite** and **Alkalsite** contain 25-32 per cent. potassium perchlorate, ammonium nitrate, trinitro-toluene, and other constituents. **Yonckite**, a Belgian explosive, contains, in addition to perchlorate, potassium nitrate and mononitronaphthalene.

Spermaceti,* tar,† naphthalene‡ and paraffin, linseed oil,§ and a solution of hydrocarbons ‖ have all been proposed for use with chlorate explosives.

The suggestion, made by Sprengel so long ago as 1871, to transport an oxygen carrier and a combustible substance separately to the place required, and there to mix them in suitable proportions immediately before use, is still acted upon in some countries. Potassium chlorate is one of the oxygen carriers used.

Winand (British Patent, 26,261, 1907) has suggested **tetranitro-methane** as an oxygen carrier for the production of explosives of the Sprengel type.

This substance should prove useful in other respects, though its volatility is a disadvantage. It can be made quite easily, without danger, and in almost theoretical amount by allowing nitric acid to react with acetic acid anhydride at ordinary temperatures (Chattaway, *Journ. Chem. Soc.*, Nov. 1910).

It is a colourless oil which solidifies to a crystalline mass, melting at 13° C. It is insoluble in water, but dissolves readily in alcohol and ether, is very stable, and does not explode on the application of heat, but distils quietly at 126° C.

Fulminate of Mercury. Azides. Primers. Percussion Caps. Detonators

The detonation of an explosive is almost always effected by the detonation of a more sensitive explosive, of which a small quantity is placed in juxtaposition with the first, and fired by mechanical shock, fuses, or electrical devices. Ordinary percussion cap composition contains a mixture of mercury fulminate, potassium chlorate and antimony sulphide to which powdered glass may be added, in order to obtain increase of sensitiveness. The caps for detonators are of pure copper, are cylindrical in shape, closed at one end, and charged with an intimate mixture of 85 per cent. mercury fulminate and 15 per cent. potassium chlorate. Detonators are made in ten sizes, numbered consecutively, and contain 0.3, 0.4, 0.54, 0.65, 0.8, 1.0, 1.5, 2.0, 2.5, or 3 g. of the detonating mixture.

Fulminic acid is the oxime of carbon monoxide, $H.O.N{=}C''$, and its mercury salt is represented by the formula $Hg\begin{matrix}O.N{=}C''\\O.N{=}C''\end{matrix}$. The latter is obtained by the action of ethyl alcohol or of methylated spirit on a solution of mercury in nitric acid. The reaction takes place in a large flask or carboy, and may require to be moderated by the addition of alcohol. It has been shown that oxides of nitrogen must be present; that acetaldehyde gives a much larger yield of fulminate than alcohol; and that 1-carbon bodies (methyl alcohol, formaldehyde) and also 3- and 4-carbon compounds give none at all.

The alcohol is first oxidised to aldehyde: this is converted by the nitrous acid present into isonitroso-acetaldehyde, and this is further oxidised to isonitroso-acetic acid. This last body is converted by nitrous fumes (by nitration followed by loss of carbon dioxide) into methyl nitrolic acid, which reacts with mercuric nitrate to give mercury fulminate:—

$$CH_3.CH_2.OH \rightarrow CH_3.CHO \rightarrow HO.N{:}CH.CHO \rightarrow HO.N{:}CH.COOH \rightarrow HO.N{:}C(NO_2).COOH \rightarrow HO.N{:}C(NO_2)H \rightarrow HO.N{:}C$$

Small grey needles of the fulminate separate, and after transference to a cloth filter are washed till acid free, and then dried in a vacuum apparatus. From 100 g. of mercury 125 g. of fulminate are obtained. The alcohol in the condensed vapours is used again. A pure white fulminate, free from metallic mercury, is obtained by adding a little hydrochloric acid and copper to the acid mixture. It is soluble in 130 times its weight of boiling water, and in ammonia, has a sp. gr. = 4.42, and when dry explodes by a moderate blow or slight friction. When detonated in a space entirely filled by it, it develops a pressure more than twice

* Hahn (British Patent, 960, 1867). † Tschirner (*ibid.*, 447, 1880).
‡ Fraenkel (*ibid.*, 13,789, 1888). § Brank (*ibid.*, 5,027, 1891).
‖ Hinly (*ibid.*, 1,969, 1882), and Lyte and Lewall (*ibid.*, 14,379, 1884).

that of nitro-glycerine treated under similar circumstances. Confinement is necessary to develop its full power, though a very slight degree of confinement is sufficient.

In the firing of smokeless powders the necessary increase in temperature is obtained by adding a combustible substance. Aluminium powder, either mixed with the fulminate or pressed in a layer on top of it, has been successfully employed by Dr Brownsdon and the King's Norton Metal Company (British Patent, 23,366, 1904). An important step in advance was made when the expensive and dangerous fulminate of mercury or its mixture with potassium chlorate was diminished in quantity to a fraction of its original amount by the use of picric acid or, much better, trinitro-toluene.

A No. 8 detonator containing 2 g. of the ordinary fulminating composition is equalled by one containing only 0.5 g. together with 0.7 g. of trinitro-toluene.

Dr Claessen (British Patent, 13,340, 1905) has shown that even better effects are obtained by the use of what he calls tetranitro-methylaniline or tetranitro-ethylaniline. These substances are really trinitro-phenyl-methyl-nitramine and trinitro-phenyl-ethyl-nitramine. The commercial name for Claessen's substance is "**tetryl**." "Tetryl" detonator No. 6 contains 0.4 g. of trinitro-phenyl-methyl-nitramine and 0.3 g. of a mixture of 87.5 per cent. mercury fulminate and 12.5 per cent. potassium chlorate.

Mercury fulminate may now be dispensed with and replaced by an even smaller quantity of an azide. Dr Lothar Wöhler finds that an ordinary No. 8 detonator is equalled by one containing 1 g. of picric acid or of trinitro-toluene and 0.023 g. of silver azide in place of the usual mercury fulminate charge of 2 g. (British Patent, 4,468, 1908).

M. Hyronimus (British Patent, 1,819, 1908) has patented the use of lead azide, $Pb(N_3)_2$, and describes a safe method of manufacturing it, founded on the process used by Wislicenus (*Ber.*, 1892, 25, 2084).

Sodamide is first prepared, and is transformed into sodium azide by warming at 300° C. in a stream of nitrous oxide gas. The sodium azide is dissolved in water, the solution is neutralised with very dilute nitric acid, and lead azide is precipitated by adding a solution of lead nitrate. The reactions which take place are represented by the following equations: (1) $Na + NH_3 = NH_2Na + H$; (2) $NH_2Na + N_2O = NaN_3 + H_2O$. The water formed decomposes part of the sodamide, thus: (3) $NH_2Na + H_2O = NH_3 + NaOH$. The reaction of the sodium azide with lead nitrate goes as follows: (4) $2NaN_3 + Pb(NO_3)_2 = Pb(N_3)_2 + 2NaNO_3$. The crystalline lead azide is washed on a filter and dried at a temperature below 100° C.

At 300° C. sodamide is fusible and sodium azide infusible; the latter as it forms absorbs the former and protects it from further action of the nitrous oxide. The sodamide is therefore incorporated with anhydrous materials like lime, magnesia, or sodium sulphate at 190°-200° C., and in this subdivided state reacts more readily with the nitrous oxide. Siliceous absorbents such as pumice stone and infusorial earth would react with the caustic soda formed in the reaction, and both delay the process and diminish the yield.

Thiele (*Ber.*, 1908, 41, 2681-2683) has obtained an almost quantitative yield of azoimide by the action of ethyl nitrite on hydrazine in presence of alkali. Hydrazine hydrate (1 molecule) is mixed with 4 N. sodium hydroxide (1½ molecules), ethyl nitrite (1½ molecules), and ether, and the mixture is allowed to remain first in ice and then at the ordinary temperature. After twenty-four hours the sodium azide is collected and washed. Hydrazine sulphate may be used with appropriate modifications. Stollé (*Ber.*, 1908, 2811-2813) has patented a similar process. The yield of azoimide obtained when a benzene solution of nitrogen chloride is shaken with a solution of hydrazine sulphate, with addition of caustic soda at intervals, is 36 per cent. (Tanatar, *Ber.*, 1899, 32, 1399).

Smokeless Powders

Smokeless powders of the present day contain, as chief constituent, nitro-cellulose alone or mixed with nitro-glycerine or some other nitro compound or inorganic oxidising agent. Attempts to use fibrous gun-cotton as a propellant were attended by failure. Dangerously high pressures were developed in the bore of the gun. It was only when the control of the rate of combustion of the explosive was made possible by gelatinisation that progress could take place.

Roughly speaking, gelatinised nitro-cellulose burns in consecutive layers in such a way that equally thick layers are consumed in equal times. With the same composition of explosive it is possible, by varying the shape and size of the unit pieces of powder in the charge, to regulate the rate of combustion of a powder so as to give the desired velocity and yet keep within the pressure limits permissible. In France, powders take the form of ribbons, in Great Britain cords, in Germany flakes and tubes, in Italy cords of square section, in the United States short multiperforated cylinders Ballistite is formed into cubes, and sporting powders abroad have in some cases a spiral shape.

For gelatinising nitro-cellulose the solvents acetone or ether alcohol are generally used, the former for gun-cotton and the latter for collodion cotton. The nitro-cellulose is used after drying by the ordinary method in drying houses, or is made anhydrous by soaking it in alcohol—first of all in alcohol which has already been used for this purpose and then in pure alcohol, squeezing the liquid out after each operation in a press. Gelatinisation of the finely powdered dry nitro-cellulose takes place in a mixing machine, after which the mixture is rolled under a pair of heavy rolls into sheets of the required thickness (0.3-0.7 mm.) which are afterwards cut up into squares and dried.

The British service powder, Cordite M.D., is a nitro-cellulose, nitro-glycerine colloid containing 65 per cent. of gun-cotton, 30 per cent. of nitro-glycerine, and 5 per cent. of mineral jelly. The percentage of nitro-glycerine was originally 58 and that of gun-cotton 37, but this produced a considerable erosive effect upon the guns which has been minimised by the adoption of the present modification without materially altering the ballistic results.

It is made as follows: Dry gun-cotton is taken in non-absorbent bags to the nitro-glycerine mixing house where the requisite amount of nitro-glycerine is added. The "paste" now in the bags is taken to a sifting house, where it is first mixed by hand in a leaden trough standing on supports and then rubbed through a sieve situated at the bottom of a bowl-shaped extension into a bag suspended beneath. Removal to the incorporating house next follows. In this is a kneading machine of the well-known Werner, Pfleiderer, & Perkins type (Fig. 245), is started after some acetone has been placed in the trough, the "paste" is then added and lastly the remainder of the acetone. After three and a half hours' incorporation the mineral jelly is added and the kneading continued for another three and a half hours. The trough is water-jacketed for cooling purposes, and a cover is placed above it to prevent loss of acetone. The cordite paste is then placed in a cylindrical mould and forced by hydraulic pressure through a die, and the long cord thus formed is wound on a metal drum or cut into lengths. It is then sent to the drying houses and dried at a temperature of about 38° C. for three to fourteen days according to the diameter of the cordite, after which it is thoroughly blended and despatched from the factory.

The finished cordite resembles a cord of gutta-percha, and varies in colour from light to dark brown. Its diameter varies according to the type of gun for which it is intended, and amounts to .0375 of an inch for the .303 rifle when it is used in bundles of sixty strands, while for heavy guns sticks of 0.40-0.50 of an inch diameter and 14 in. long are used. A smaller charge is required to produce a given muzzle velocity with cordite than with gunpowder, and temperature differences do not affect its ballistic properties much more than in the case of the latter. It is safe to handle, is very insensitive to shock, can be burnt away in considerable quantities without explosion, and retains its stability for considerable periods under the most varied climatic conditions. Its erosive effect upon guns is greater than that of gunpowder, and differs in its nature from that produced by the latter, which furrows the metallic surface, while cordite sweeps the surface smoothly away for a shorter distance.

The annexed figure, taken from Professor V. B. Lewes's paper read before the Society of Arts, and due to Dr W. Anderson, F.R.S., shows graphically the pressures given by cordite and by black powder in the 6-in. gun (Fig. 248).

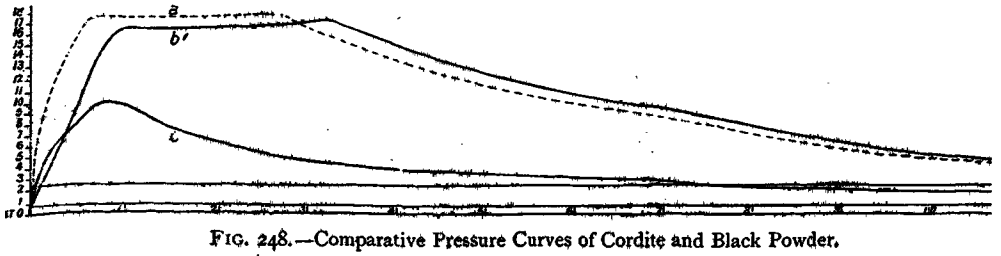

FIG. 248.—Comparative Pressure Curves of Cordite and Black Powder.

a, Charge, 48 lbs. powder; *b*, Charge, 13 lbs. 4 oz. cordite; *c*, Charge, 13 lbs. 4 oz. powder. Weight of projectile, 100 lbs. in 6-in. gun. M.V. cordite = 1,960 ft. per sec.

A problem of great economic importance, that of the profitable recovery of solvent from the gelatinised explosive during drying, has been solved in recent years. Dr Robert Robertson and Mr Wm. Rintoul (British Patent, 25,993, 1901) have worked out, at Waltham Abbey, the process now used for recovering acetone from the atmosphere of cordite drying houses.

The accompanying drawing of the absorption apparatus (Fig. 249), together with the following brief description, will serve to indicate the method of working. The interiors of the drying houses are

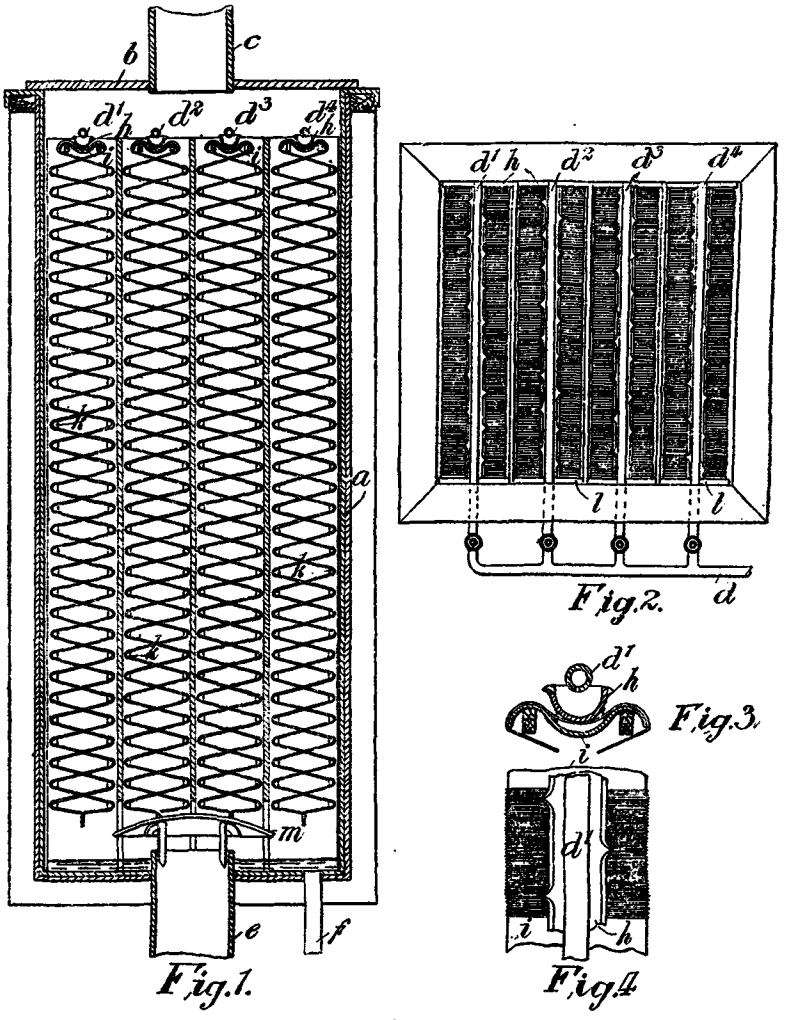

FIG. 249.—Section, Plan, and details of an Absorption Tower used in Robertson and Rintoul's Acetone Recovery Process.

connected by zinc pipes to a central absorption apparatus consisting of a series of towers of rectangular section. A concentrated solution of sodium bisulphite is run down these towers, and is distributed so as to descend by way of the woollen or other fibres which are arranged in zigzag fashion on wooden frames, and at the same time a Root's blower or exhaust fan aspirates the acetone-laden air of the drying houses through the towers in series, the air current passing up the tower while the bisulphite solution flows down. The liquors which have collected at the bottom of the last tower and have met the poorest acetone mixture are blown by compressed air elevators to the tank connected with the top of the second tower, while fresh bisulphite solution continually descends

the last tower. The partially saturated bisulphite solution descends the second tower, and afterwards, in the same way, the remaining towers of the series; the saturated solution obtained from the first tower, that up which the air current first passes, is distilled, and the distillate is rectified over caustic soda. The residual bisulphite solution is used again.

Bouchaud-Praeciq (British Patent, 6,075, 1905) has described a process for alcohol ether recovery in which the vapours are aspirated first through a cooling and drying vessel containing a mixture of calcium carbide and sodium, and thence to an absorbing chamber, charged with pumice stone, down which sulphuric acid flows. The liquid is distilled at a low temperature or under reduced pressure for recovery of the solvent.

Solenite is an Italian nitro-glycerine, nitro-cellulose powder, containing 30 parts of nitro-glycerine, 40 parts of "insoluble" and 30 parts of "soluble" nitro-cellulose, the two latter having an average of 12.6 per cent. of nitrogen. Acetone is used for promoting the solution of the "insoluble" nitro-cellulose.

Ballistite is another nitro-glycerine, nitro-cellulose powder the manufacture of which differs from those already given. "Soluble" nitro-cellulose, in the form of a fine powder, is suspended in fifteen times its own bulk of hot water, and nitro-glycerine is added, the mixture being stirred by means of compressed air (Lundholm & Sayers, British Patent, 10,376, 1889). The water acts as a carrier and enables the nitro-glycerine to gelatinise the nitro-cellulose. The paste resulting is freed from water in a centrifugal machine and allowed to ripen. It is then brought under heated rolls (122°-140° F.), weighted to exert a pressure of 100 atmospheres. and the sheets thus obtained are cut up into flakes, cubes, strips, etc., as required.

Sporting powders are of two kinds, the so-called bulk powders, consisting of loose granules, coated or hardened by means of a solvent, and the so-called condensed powders, gelatinised throughout and made in practically the same way as military flake powders. A powder of an intermediate type, the Walsrode powder, for instance, is made by first gelatinising throughout, and then treating with water or steam. In this way granules are formed and part of the solvent is driven out again, leaving a "bulky" but hard grained powder behind. The bulk powders are supposed to just fill a cartridge used in the old black-powder gun, the condensed powders are made for modern weapons. The usual bulk powders are composed of collodion cotton mixed with potassium or barium nitrate, and generally worked up in an incorporating mill or drum. The mixture is then either sprinkled with water in a rotating drum so as to form grains, or may be pressed and then broken into grains, the solvent being sprinkled over when the grains are already formed.

Smokeless powder gives a strong luminous flame which in military operations will disclose the position of an attacking force. The flame owes its luminosity to incandescent solid particles, and to the sudden combustion, under pressure, of gases which have escaped complete oxidation in the gun, but are still capable of uniting with oxygen. Many attempts to secure absence of flame have been based on the principles applied to the making of safety explosives for coal mines. Sodium bicarbonate and cyanamide, for instance, are added to produce a cooling effect. The following have been the subjects of patents: Vaseline (British Patent, 19,773, 1900); Vaseline and alkali bicarbonate (D.R. Patent, 175,399, 1903); Diethyldiphenylurea (D.R. Patent, 194,874, 1906); Cyanamide (D.R. Patent, 201,215, 1902); Tartrates (British Patent, 15,566, 1905); Olive oil (British Patent, 15,565, 1905); Salts of dibasic organic acids and oils, fats or resins (British Patent, 19,408, 1906); Soaps (D.R. Patent, 195,486, 1907).

The nitro-cellulose used in modern explosives has a tendency to decompose under conditions to which it may frequently be subjected before it is actually used in the gun, and in its gelatinised condition retains small quantities of the solvent which has been used to produce the powder, in spite of the prolonged drying at somewhat elevated temperatures which it has undergone. The removal of residual solvent is important if constant ballistic qualities are to be obtained. Water treatment, followed by drying, has been resorted to in some cases, but wherever heating is necessarily prolonged there is considerable risk of impairing stability.

At the same time it may be pointed out that a heat treatment will sometimes apparently improve a powder, and may actually do so if volatile catalysts alone are in question.

Stability must be carefully tested at regular intervals during storage. Special additions are frequently made during manufacture for the purpose of removing incipient acidity. Aniline, for example, is added to ballistite in Italy, and diphenylamine, which is used in France, acts not only as a so-called "stabiliser," but as an indicator, owing to the change in colour produced by nitrogen oxides. These additions, however, delay deterioration under adverse storage conditions for a short time only.

The composition of a few smokeless powders will be found in the appendix.

The writer of the article desires to acknowledge his indebtedness to the following works:—

"The Manufacture of Explosives," by the late Oscar Guttmann, F.I.C. Whittaker & Co., 1895.
"Twenty Years' Progress in Explosives," by the same author. 1909.
"A Handbook of Modern Explosives," by M. Eissler. Crosby Lockwood & Son, 1897.
"Nitro-Explosives," by P. Gerald Sanford, F.I.C., F.C.S. Crosby Lockwood & Son, 2nd edition, 1906.
"Die Explosivstoffe,"—"Nitroglyzerin und Dynamit" (1908), "Ammonsalpetersprengstoffe" (1909), "Chloratsprengstoffe" (1910); by Dr Richard Escales. Veit & Co., Leipzig.
"New Methods of Testing Explosives," by C. E. Bichel. Charles Griffin & Co. Ltd., 1905
Dr Dammer's "Chemische Technologie der Neuzeit." Article on "Explosivstoffe" by Dr Richard Escales. Ferdinand Enke, 1910.
Allen's "Commercial Organic Analysis," new edition. Article by A. Marshall, F.I.C., on "Modern Explosives." 1910.
The Journal of the Chemical Society; The Journal of the Society of Chemical Industry; The Chemical Trade Journal; Zeitschrift für das gesamte Schiess- und Sprengstoffwesen; Zeitschrift für angewandte Chemie; Chemiker Zeitung.

Observations on the Testing of Explosives

All materials used in the manufacture of explosives must conform to rigid specifications, which are framed with a view to obtaining a uniform supply free from matters which would affect injuriously both safe and economical working and stability, chemical and physical, of the finished product.

The proximate ingredients of an explosive mixture are subjected to a searching examination before the process of incorporation takes place, and the homogeneous mixture obtained is afterwards tested with regard to (1) proximate composition, (2) chemical stability, (3) capacity for retaining original physical properties under conditions more adverse than those likely to be encountered during storage or shipment, (4) mechanical energy, (5) safety under working conditions, *e.g.*, sensitiveness to shock and friction and liability to ignite mixtures of air and coal-gas, into which sample cartridges are fired.

It is impossible to do more than indicate briefly a few of the more important points connected with the first two tests. For full details the larger works must be consulted.

Proximate Analysis.—Moisture and residual solvent, in the case of nitro-glycerine explosives, are determined by Marshall's modification of L. W. Dupré's method (L. W. Dupré, *Chemiker Zeitung*, 540, 1901, and Marshall, *Journ. Soc. Chem. Ind.*, 154, 1904). P. V. Dupré (*Analyst*, 1906, 31, 213) estimates water in the volatile matter by passing it through a layer of calcium carbide and measuring the acetylene generated.

Other Constituents.—2 g. of the sample, weighed out into a folded filter paper, are extracted with ether (sp. gr. 0.720) in a Soxhlet apparatus. The extract may contain nitro-glycerine, resin, camphor, sulphur, mineral jelly, or paraffin. In the case of cordite the nitro-glycerine and mineral jelly thus extracted are separated by repeated digestion with aqueous methyl alcohol (80 parts by volume of absolute methyl alcohol to 20 parts by volume of water), which leaves the mineral jelly undissolved. The contents of the filter paper are now extracted with water, and the residue left on evaporating the aqueous solution is examined for ammonium nitrate, potassium chlorate, barium nitrate, and soluble combustible substances. In the insoluble residue aluminium is determined by dissolving it in hydrochloric acid and precipitating it from solution as hydrate. Extraction with acetone will remove nitro-celluloses. The different kinds of carbon may be distinguished in the residue by their behaviour on heating. Wood fibre is recognised by the microscope and by the presence of tannin in an extract, due to bark and nut-galls. Sulphur is transformed into sulphate by oxidation with nitre and potassium chlorate.

Nitro-glycerine, before being used as an ingredient of an explosive mixture, is tested with regard to (1) percentage of nitrogen, (2) alkalinity, (3) moisture, and (4) stability. A direct method of estimating the percentage of nitro-glycerine (usually determined by difference) in an explosive mixture is that of Silberrad, Phillips, and Merriman (*Journ. Soc. Chem. Ind.*, 25, 628).

Nitro-cellulose is examined for percentage of nitrogen by means of the Lunge nitrometer or by the Schultze-Tiemann process (see Marshall's article, Allen's "Commercial Organic Analysis," 4th edition, 1910, vol. iii.). An important paper on nitrogen estimation is that of Berl and Jurrissen (*Zeits. Schiess-Sprengstoffwesen*, 1910, 4, 61). Nitro-cellulose is also examined as regards solubility in ether alcohol, amount of unnitrated fibre, matter insoluble in acetone, ash and inorganic matter, degree of alkalinity, presence of sulphuric esters, viscosity of 1 per cent. solutions in ether alcohol or acetone, and stability.

Picric Acid is tested for the presence of resinous and tarry matters, sulphuric acid, hydrochloric acid, oxalic acid, and their salts. General impurities and adulterations, *e.g.*, oxalic acid, nitrates, picrates, boric acid, alum, sugar, etc., remain insoluble on shaking the sample with ether, and may be further examined. The melting point of the pure acid is 122° C. Dinitrophenol may be estimated by Allen's process (*Journ. Soc. Dyers, etc.*, 4, 84). Mineral or non-combustible matter must not exceed 0.3 per cent. by weight.

Fulminate of Mercury is white or light grey in colour, should dissolve readily and completely, or almost completely, in ammonia or concentrated hydrochloric acid and in potassium cyanide solution. It is examined for metallic mercury, mercurous compounds, and oxalates (see Solonina, *Zeits. Schiess-Sprengstoffwesen*, 1910, 3, 41, and 1910, 4, 67).

Cap Composition [$(CNO)_2Hg$; Sb_2S_3; $KClO_3$] is analysed according to Brownsdon's method (*Journ. Soc. Chem. Ind.*, xxiv., April 1905), or that of Messrs F. W. Jones and F. A. Willcox (*Chem. News*, Dec. 11, 1896). The latter dissolve the fulminate by means of acetone saturated with ammonia gas, and afterwards remove the potassium chlorate by extraction with water.

Stability Tests

Most of the numerous tests which have been used or suggested are based upon the detection or measurement of nitrogen oxides evolved when the explosive is heated. They are classified as (1) "Trace Tests," in which the time required to produce a definite colour upon a sensitive test paper suspended over the heated explosive is measured, the temperature being either 160° F. or 180° F.; (2) "Fume Tests," carried out at higher temperatures (100°-135° C.), in which the time elapsing before fumes appear, or before a less sensitive reagent is affected, is measured; and (3) quantitative tests, made at the same temperatures as those attained in "Fume Tests," in which the amount of decomposition products evolved in a given somewhat extended time is determined. No single test has been devised yet which can be relied upon to indicate the probable duration of stability, even under normal conditions. A committee, appointed by the Home Office, has the whole question of the Heat Test under consideration, but has not yet published a report. A bare summary of stability tests follows.

Trace Tests

1. **Abel Heat Test** (Explosives Act, 1875).—The test paper is impregnated with potassium iodide and starch. (See paper by Robertson and Smart, *Journ. Soc. Chem. Ind.*, Feb. 15, 1910). For detection of mercuric chloride or metallic mercury, the presence of which renders the Heat Test valueless, see method adopted by F. H. and P. V. Dupré, and described in the Annual Report of H.M. Inspectors of Explosives for 1907, p. 17. Hargreaves and Rowe (*Journ. Soc. Chem. Ind.*, 1907, 26, 813) have worked out a method for the microscopic detection of mercury.
2. Test papers may be impregnated with zinc iodide and starch.
3. **Guttmann's Test** (*Journ. Soc. Chem. Ind.*, 16, 1897).—Diphenylamine sulphate is the indicator used in this case. The test was claimed to be independent of the presence of solvent or of mercuric chloride.
4. **Spica's Test.**—The indicator used is *m*-phenylene diamine hydrochloride (with cane sugar).

Fume Tests

1. Vieille Test
2. German 135° Test

See Sy (*Journ. Franklin Inst.*, 1908, 166, pp. 249, 321, 433); also *Journ. Amer. Chem. Soc.*, 1903, 25, 550.

Explosion Test. The temperature is noted at which 0.1 g. of the sample explodes on being heated at a uniform rate of 5° C. per minute from 100° C.

Waltham Abbey Silvered Vessel Test. See paper by Sir F. L. Nathan, R.A. Also article on "Modern Explosives" by Marshall in Allen's "Commercial Organic Analysis."

Quantitative Tests

The Will Test.—See Will ("Mittheilungen der Centralstelle," Neu Babelsberg, 1900, 2), and Robertson (*Journ. Soc. Chem. Ind.*, 1901, 20, 609; *Trans. Chem. Soc.*, 1907, 764, and 1909, 1, 241.

Bergmann and Junk Test (*Zeits. Angew. Chem.*, 1904, 982).

Sy's test for nitro-cellulose powders (*Journ. Amer. Chem. Soc.*, 1905, 25, 550).

Composition of Some Explosives in Common Use

Ordinary Dynamite.

Nitro-glycerine	75 per cent.
Kieselguhr	25 ,,

Amois.

Nitrate of ammonia	90 per cent.
Chlor-dinitrobenzene	5 ,,
Wood pulp	5 ,,

Ammonia Nitrate Powder.

Nitrate of ammonia	80 per cent.
Chlorate of potash	5 ,,
Nitro-glucose	10 ,,
Coal-tar	5 ,,

Celtite.

Nitro-glycerine	56.0 to 59.0 parts.
Nitro-cotton	2.0 ,, 3.5 ,,
KNO_3	17.0 ,, 21.0 ,,
Wood meal	8.0 ,, 9.0 ,,
Ammonium oxalate	11.0 ,, 13.0 ,,
Moisture	0.5 ,, 1.5 ,,

Atlas Powders.

Sodium nitrate	2 per cent.
Nitro-glycerine	75 ,,
Wood pulp	21 ,,
Magnesium carbonate	2 ,,

Dualine.

Nitro-glycerine	50 per cent.
Sawdust	30 ,,
Nitrate of potash	20 ,,

Vulcan Powder.

Nitro-glycerine	30.0 per cent.
Nitrate of soda	52.5 ,,
Sulphur	7.0 ,,
Charcoal	10.5 ,,

Vigorite.

Nitro-glycerine	30 per cent.
Nitrate of soda	60 ,,
Charcoal	5 ,,
Sawdust	5 ,,

Rendrock.

Nitrate of potash	40 per cent.
Nitro-glycerine	40 ,,
Wood pulp	13 ,,
Paraffin or pitch	7 ,,

Hercules Powders.

Nitro-glycerine	75.00 to 40.00 per cent.
Chlorate of potash	1.05 ,, 3.34 ,,
Sugar	1.00 ,, 15.66 ,,
Nitrate of potash	2.10 ,, 31.00 ,,
Carbonate of magnesia	20.85 ,, 10.00 ,,

Carbo-Dynamite.

Nitro-glycerine	90 per cent.
Charcoal	10 ,,

Geloxite (Permitted List).

Nitro-glycerine	64 to 54 parts.
Nitro-cotton	5 ,, 4 ,,
Nitrate of potash	22 ,, 13 ,,
Ammonium oxalate	15 ,, 12 ,,
Red ochre	1 ,, 0 ,,
Wood meal	7 ,, 4 ,,

The wood meal to contain not more than 15 per cent. and not less than 5 per cent. moisture.

Giant Powder.

Nitro-glycerine	40 per cent.
Sodium nitrate	40 ,,
Rosin	6 ,,
Sulphur	6 ,,
Kieselguhr	8 ,,

Dynamite de Trauzl.

Nitro-glycerine	75 parts.
Gun-cotton	25 ,,
Charcoal	2 ,,

Rhenish Dynamite.

Solution of N.-G. in naphthalene	75 per cent.
Chalk or barium sulphate	2 ,,
Kieselguhr	23 ,,

Ammonia Dynamite.

Ammonium nitrate	75 parts.
Paraffin	4 ,,
Charcoal	3 ,,
Nitro-glycerine	18 ,,

Blasting Gelatine.

Nitro-glycerine	93 per cent.
Nitro-cotton	3 to 7 ,,

Gelatine Dynamite.

Nitro-glycerine	71 per cent.
Nitro-cotton	6 ,,
Wood pulp	5 ,,
Potassium nitrate	18 ,,

Gelignite.

Nitro-glycerine	60 to 61 per cent.
Nitro-cotton	4 ,, 5 ,,
Wood pulp	9 ,, 7 ,,
Potassium nitrate	27 ,,

Forcite.

Nitro-glycerine	49.0 per cent.
Nitro-cotton	1.0 ,,
Sulphur	1.5 ,,
Tar	10.0 ,,
Sodium nitrate	38.0 ,,
Wood pulp	0.5 ,,

(The N.-G., etc., varies.)

TONITE No. 1.

Gun-cotton	52 to 50 parts.
Barium nitrate	47 ,, 40 ,,

TONITE No. 2.

Contains charcoal also.

TONITE No. 3.

Gun-cotton	18 to 20 per cent.
$Ba(NO_3)_2$	70 ,, 67 ,,
Dinitro-benzol	11 ,, 31 ,,
Moisture	0.5 ,, 1 ,,

CARBONITE.

Nitro-glycerine	17.76 per cent.
Nitro-benzene	1.70 ,,
Soda	0.42 ,,
KNO_3	34.22 ,,
$Ba(NO_3)_2$	9.71 ,,
Cellulose	1.55 ,,
Cane Sugar	34.27 ,,
Moisture	0.36 ,,
	99.99

ROBURITE.

Ammonium nitrate	86 per cent.
Chlor-dinitro-benzol	14 ,,

FAVERSHAM POWDER.

Ammonium nitrate	85 per cent.
Dinitro-benzol	10 ,,
Trench's flame-extinguishing compound	5 ,,

FAVIERITE No. 1.

Ammonium nitrate	88 per cent.
Dinitro-naphthalene	12 ,,

FAVIERITE No. 2.

No. 1 powder	90 per cent.
Ammonium chloride	10 ,,

BELLITE.

Ammonium nitrate	5 parts.
Meta-dinitro-benzol	1 ,,

PETROFRACTEUR.

Nitro-benzene	10 per cent.
Chlorate of potash	67 ,,
Nitrate of potash	20 ,,
Sulphide of antimony	3 ,,

SECURITE.

Mixtures of Meta-dinitro-benzol and Nitrate of ammonia	26 per cent. 74 ,,

RACK-A-ROCK.

Potassium chlorate	79 per cent.
Mononitro-benzene	21 ,,

OXONITE.

Nitric acid (sp. gr. 1.5)	54 parts.
Picric acid	46 ,,

EMMENSITE.

Emmens' acid	5 parts.
Ammonium nitrate	5 ,,
Picric acid	6 ,,

BRUGÈRE POWDER.

Ammonium picrate	54 per cent.
Nitrate of potash	46 ,,

DESIGNOLLE'S TORPEDO POWDERS.

Potassium picrate	55 to 50 per cent.
Nitrate of potash	45 ,, 50 ,,

STOWITE.

Nitro-glycerine	58.0 to 61 parts.
Nitro-cotton	4.5 ,, 5 ,,
Potassium nitrate	18.0 ,, 20 ,,
Wood meal	6.0 ,, 7 ,,
Oxalate of ammonia	11.0 ,, 15 ,,

The wood meal shall contain not more than 15 per cent. and not less than 5 per cent. by weight of moisture. The explosive shall be used only when contained in a non-waterproofed wrapper of parchment.—No. 6 detonator.

FAVERSHAM POWDER.

Ammonium nitrate	93 to 87 parts.
Trinitro-toluol	11 ,, 9 ,,
Moisture	1 ,,

KYNITE.

Nitro-glycerine	24.0 to 26.0 parts.
Wood pulp	2.5 ,, 3.5 ,,
Starch	32.5 ,, 3.5 ,,
Barium nitrate	31.5 ,, 34.5 ,,
$CaCo_3$	0 ,, 0.5 ,,
Moisture	3.0 ,, 6.0 ,,

Must be put up only in waterproof parchment paper, and No. 6 electric detonator used.

REXITE.

Nitro-glycerine	6.5 to 8.5 parts.
Ammonium nitrate	64.0 ,, 68.0 ,,
Sodium nitrate	13.0 ,, 16.0 ,,
Trinitro-toluol	6.5 ,, 8.5 ,,
Wood meal	3.0 ,, 5.0 ,,
Moisture	0.5 ,, 1.4 ,,

Must be contained in waterproof case (stout paper), waterproofed with resin and ceresin.—No. 6 detonator.

WITHNELL POWDER.

Ammonium nitrate	88 to 92 parts.
Trinitro-toluol	4 ,, 6 ,,
Flour (dried at 100° C.)	4 ,, 6 ,,
Moisture	0 ,, 15 ,,

Only to be used when contained in a linen paper cartridge, waterproofed with carnauba wax, paraffin—No. 7 detonator used.

PHŒNIX POWDER.

Nitro-glycerine	28 to 31 parts.
Nitro-cotton	0 ,, 1 ,,
Potassium nitrate	30 ,, 34 ,,
Wood meal	33 ,, 37 ,,
Moisture	2 ,, 6 ,,

Smokeless Powders

CORDITE.

Nitro-glycerine	58 per cent.	+ or − .75
Nitro-cotton	37 ,,	+ or − .65
Vaseline	5 ,,	+ or − .25

CORDITE M.D.

Nitro-glycerine	30 per cent.	+ or − 1
Nitro-cotton	65 ,,	+ or − 1
Vaseline	5 ,,	+ or − 0.25

Analysis of:—By W. Macnab and A. E. Leighton.

E. C. POWDER.

Nitro-cotton	79.0 per cent.
Potassium nitrate	4.5 ,,
Barium nitrate	7.5 ,,
Camphor	4.1 ,,
Wood meal	3.8 ,,
Volatile matter	1.1 ,,

WALSRODE POWDER.

Nitro-cotton	98.6 per cent.
Volatile matter	1.4 ,,

KYNOCH'S SMOKELESS.

Nitro-cotton	52.1 per cent.
Dinitro-toluol	19.5 ,,
Potassium nitrate	1.4 ,,
Barium nitrate	22.2 ,,
Wood meal	2.7 ,,
Ash	0.9 ,,
Volatile matter	1.2 ,,

SCHULTZE.

Nitro-ligrin	62.1 per cent.
Potassium nitrate	1.8 ,,
Barium nitrate	26.1 ,,
Vaseline	4.9 ,,
Starch	3.5 ,,
Volatile matter	1.0 ,,

IMPERIAL SCHULTZE.

Nitro-lignin	80.1 per cent.
Barium nitrate	10.2 ,,
Vaseline	7.9 ,,
Volatile matter	1.8 ,,

CANNONITE.

Nitro-cotton	86.4 per cent.
Barium nitrate	5.7 ,,
Vaseline	2.9 ,,
Lampblack	1.3 ,,
Potassium ferrocyanide	2.4 ,,
Volatile matter	1.3 ,,

AMBERITE.

Nitro-cotton	71.0 per cent.
Potassium nitrate	1.3 ,,
Barium nitrate	18.6 ,,
Wood meal	1.4 ,,
Vaseline	5.8 ,,

SPORTING BALLISTITE.

Nitro-glycerine	37.6 per cent.
Nitro-cotton	62.3 ,,
Volatile matter	0.1 ,,

STATISTICS OF EXPORTS AND IMPORTS OF AMMUNITION, HIGH EXPLOSIVES, ETC., FOR THE UNITED KINGDOM, FOR THE YEARS 1906 AND 1910

EXPORTS.

Material.	1906.		1910.	
	Quantities	Value.	Quantities.	Value.
	Cwt.	£	Cwt.	£
Cordite and other smokeless propellants	11,894	172,864	12,720	172,399
Gunpowder	65,241	176,846	71,788	176,743
High explosives—				
Dynamite and other high explosives	149,035	898,208	143,931	726,457
Small arms ammunition—				
Military	84,525	413,530	11,454	82,840
Sporting			61,117	253,009
Fuzes, tubes, primes, etc.	1,253	38,866	1,478	57,444
	Thousands.		Thousands.	
Percussion caps	281,064	22,712	326,397	24,864
Metal cartridge cases other than small arms ammunition—	Cwt.		Cwt.	
Filled	10,122	103,342	13,281	134,803
Empty	789	7,234	2,094	17,449
Shot and shell	22,193	110,430	45,959	163,340
Rockets and other combustibles, explosives, and ammunition, of natures not named above	...	301,820	...	407,254
Total for ammunition	...	2,245,852	...	2,216,602

IMPORTS.

Cordite and other smokeless propellants	678	10,824	591	8,641
Gunpowder	4,744	10,915	4,932	10,934
High explosives—				
Dynamite and other high explosives	31,774	121,571	9,117	37,748
Small arms ammunition—				
Military	7,742	50,002	24	334
Sporting			7,507	44,562
Fuses, tubes, primes, etc.	1,943	6,772	2,006	6,173
	Thousands.		Thousands.	
Percussion caps	24,571	2,241	16,668	1,962
Metal cartridge cases other than small arms ammunition—	Cwt.		Cwt.	
Filled	295	1,538	...	...
Empty	354	1,720	...	...
Shot and shell	4,225	21,185	607	2,209
Rockets and other combustibles, explosives, and ammunition, of natures not named above	...	61,036	...	47,658
Total for ammunition	...	287,804	...	160,221

THE IMPORTS AND EXPORTS OF EXPLOSIVES FOR THE UNITED STATES ARE GIVEN IN THE FOLLOWING STATISTICS

IMPORTS INTO THE UNITED STATES FROM ALL SOURCES.

Material.	1906.		1909.	
	Quantities, in Lbs.	Value, in Dollars.	Quantities, in Lbs.	Value, in Dollars.
Caps, blasting and percussion (dutiable)	...	14,084	...	8,696
Cartridges (dutiable)	...	124,955	...	68,893
Firecrackers (dutiable)	4,919,122	366,776	5,927,003	343,348
Fireworks (dutiable)	...	21,931	...	52,806
Fulminates and all like articles (dutiable)	...	199,095	...	182,482
Fuse, mining and blasting (dutiable)	...	10,221	...	15,675
All other explosives (dutiable)	...	128,454	...	266,002 (789,635 in 1910)
Totals	...	865,516	...	937,902

EXPORTS FROM THE UNITED STATES.

Material.	1906.		1907.		1908.		1909.		1910.	
	Quantities, in Lbs.	Value, in Dollars.	Quantities, in Lbs.	Value, in Dollars.	Quantities, in Lbs.	Value, in Dollars.	Quantities, in Lbs.	Value, in Dollars.	Quantities, in Lbs.	Value, in Dollars.
Cartridges	...	...	...	...	...	1,745,007	...	2,132,394	...	2,521,749
Dynamite	...	...	...	...	...	793,433	...	615,641	...	1,636,225
Gunpowder	891,379	124,322	472,159	78,620	2,051,356	315,494	690,851	136,822	1,218,541	249,917
All other explosives (including cartridges and dynamite prior to 1908)	...	3,443,716	...	4,003,782	...	851,583	...	593,857	...	944,772
Totals	...	3,568,038	...	4,082,402	...	3,705,517	...	3,478,714	...	5,352,663

List of Principal Explosives used at Mines and Quarries in the United Kingdom under the Coal Mines Regulation Act, the Metalliferous Mines Act, and the Quarries Act, in 1909

Permitted Explosives.

Name of Explosive.	Quantity Used.	Percentage of Total.	Name of Explosive.	Quantity Used.	Percentage of Total.
	Lbs.			Lbs.	
Bobbinite	1,118,459	13.2	Brought forward	8,255,446	97.0
Arkite	750,718	8.8	Celtite	38,639	0.5
Monobel	739,282	8.7	Amvis	34,564	0.4
Ammonite	554,371	6.5	Geloxite	30,527	0.4
Samsonite	506,991	6.0	†Steelite	29,840	0.3
Saxonite	504,146	5.9	Tutol	16,668	0.2
Rippite	485,058	5.7	Fracturite	16,382	0.2
Roburite	478,823	5.6	Normanite	15,178	0.2
Westfalite	444,770	5.2	Dominite	13,754	0.2
Bellite	443,181	5.2	Minite	9,576	0.1
Carbonite	431,721	5.1	Cambrite	9,435	0.1
Stowite	258,822	3.0	Aphosite	7,600	0.1
Faversham powder	227,564	2.7	Swalite	7,505	0.1
*Ammonal	214,543	2.5	Dragonite	6,050	
Albionite	202,769	2.4	Amasite	4,000	
Excellite	176,235	2.1	Kynite	3,979	
Rexite	167,164	2.0	Nobel ammonia powder	1,900	
Abbcite	120,106	1.4	Ripping ammonal	445	
Permonite	119,992	1.4	Odite	396	17,118 0.2
Cornish powder	99,079	1.2	Dahmenite	122	
Negro powder	62,566	0.7	Electronite	100	
St Helens powder	60,552	0.7	Phœnix powder	50	
Oaklite	45,699	0.5	Britonite	40	
Kolax	42,835	0.5	Withnell powder	20	
			Haylite	16	
Carried forward	8,255,446	97.0	Total	8,502,232	100.0

* This includes the non-permitted ammonal.
† Includes colliery steelite and non-permitted steelite.

All Explosives.

Name of Explosive.	Quantity Used.	Percentage of Total.
	Lbs.	
Permitted explosives	8,502,232	28.3
Gunpowder	17,595,475	58.5
Gelignite	3,085,529	10.2
Blasting gelatine	616,436	2.0
Gelatine dynamite		
Cheddite	123,531	0.4
Dynamite	117,260	0.4
Various	51,424	0.2
Total	30,091,887	100.0

SECTION XXIII

The Industry of Photographic Chemicals

THE INDUSTRY OF PHOTOGRAPHIC CHEMICALS

By G. Martin, Ph.D., M.Sc

LITERATURE

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The manufacture of photographic chemicals is a modern industry of great and rapidly growing importance.

We can only give in this place an account of the more important substances especially manufactured for photographic purposes. Chemicals which are widely employed in other industries—such as sodium thiosulphate, salts of gold, silver, platinum, etc.—cannot be discussed here, since an account of these technically important salts will be given in the second volume of this work.

Statistics.—The United States imported in 1910—Moving picture films, 12,830,000 lin. ft., of value $771,000. Photographic plates and other films, value $416,000. Photographic paper, value $762,000.

The American export of **photographic goods** is shown by the following figures:—

1906	1907	1908	1909	1910
$256,000	$1,090,000	$2,840,000	$4,185,000	$4,765,000

The United Kingdom in 1913 *exported* £1,065,700 of photographic materials. The *import* in 1913 was £2,372,000. The value of the photographic materials (plates, paper, and films), produced in Great Britain in 1907 was £909,000.

Although exact statistics are at present unobtainable, the magnitude of the industry of photographic chemicals may be gauged by the fact that one factory in England alone orders its potassium bromide in 30-ton lots, and that one company is the largest user of silver except a Government mint! The production of the biggest English photographic paper factories runs to *miles*, and of plates to *acres* per day. Many thousands of workers are employed in the industry.

CHEMICALS EMPLOYED IN THE MANUFACTURE OF PHOTOGRAPHIC PLATES AND FILMS

Dry Plates.—The ordinary dry plate is a specially selected best quality thin glass sheet, covered with an extremely light-sensitive layer of silver bromide particles suspended in gelatine. The glass, cleaned by automatic machinery by brushing and spraying with soda and water, is coated with a substratum consisting of a weak solution of gelatine containing chrome alum, which causes the emulsion to adhere to the glass and prevents "frilling," then dried by hot air and coated with the sensitive emulsion by a special machine, dried in a special room, cut to the proper size by machinery, examined for defects by red light, and packed.

The Emulsion is made by adding a concentrated solution of silver nitrate to a potassium bromide solution containing gelatine. Negative emulsions usually have a small percentage of KI added to the gelatine, while diapositive and "gaslight" paper emulsions consist chiefly of silver chloride with a very little bromide. After mixing, the emulsion is "ripened" by keeping at a high temperature for some time, or by digesting at a lower temperature with

ammonia, then it is cooled by ice until it sets to a jelly, forced by hydraulic pressure through small holes in a metal plate, and the threads thus produced washed free from the KNO_3 (formed thus: $AgNO_3 + KBr = KNO_3 + AgBr$). The "fastness" of the plate depends upon the size of the grains of AgBr—the larger the grain the faster the plate.

The British Patent, No. 1,689 of 1908, describes a plate containing derivatives of hydrazine, which, it is stated, cannot be over-exposed.

Collodion Wool is simply nitrated cotton, the manufacture of which is described on pp. 207, 624.

Collodion is its solution in a mixture of alcohol and ether, usually containing 5 per cent of wool.

The solvent rapidly evaporates in the air, leaving a skin. It is used for making light-sensitive surfaces in the wet plate process, in the manufacture of silver bromide collodion emulsions, and for making light filters.

Celluloid is used for the manufacture of films, cinematographic pictures, etc., also as a protective covering for pictures, being for the latter purpose coated with an adhesive. For the manufacture of celluloid see p. 208.

Cellite, or **Cellulose Acetate**, is used for the same purposes as celluloid; although dearer it has the great advantage over celluloid that it is practically non-inflammable. For its manufacture see pp. 216, 210.

Gelatine is largely used for the manufacture of dry plates, and for making light-sensitive emulsions of silver halides. For the manufacture and properties of gelatine see p. 595.

The ordinary dry plate is covered with an extremely light-sensitive layer of silver bromide particles suspended in gelatine. The gelatine on the plate may be hardened after development by soaking in a solution of formalin or of alum.

Albumen and **Casein** used in the manufacture of photographic papers. For manufacture and properties of albumen see p. 597, and for casein, p. 79.

DYES USED IN THE PREPARATION OF PHOTOGRAPHIC PLATES AND FILMS

Silver halides are most sensitive to blue and violet light rays, and least sensitive to red rays. Various dyes are used to render silver halides treated with them more sensitive to red, yellow, and green rays, so that the true colours are better reproduced in the resulting picture than would otherwise be possible.

The dye may be added to the sensitive emulsion either before pouring it on to the plate, or it is applied to the dry plate after manufacture by immersing it in a dilute solution of the dye and then allowing the plate to dry. For example, in the case of cyanin dyes a solution containing 1 part dye : 1,000 water is used, and 2-4 c.c. of this solution is added to 100 c.c. of a mixture of 40 c.c. alcohol + 60 c.c. water. The plates are bathed in the solution for two to three minutes and then dried at 18°-24° for ten minutes—the whole operation being carried out in the dark. Plates which have been thus rendered almost equally sensitive to all the rays of the spectrum are termed "**panchromatic**," while those which are especially sensitised for green and yellow—very important for landscape pictures—are the so-called "**orthochromatic**" plates.

When ortho plates are bathed in pinacyanol, the plate is hypersensitised, and exposure necessary reduced to one-fourth its original amount. The plate is immersed for ten minutes in the bath, which consists of 1 milligram of pinacyanol in 1 c.c. alcohol + 1,000 c.c. H_2O + 2 drops NH_3.

Lumière's **autochrome** plates give very beautiful results. The plates are prepared with a sensitive gelatine film and a multicolour light filter composed of blue, green, and red starch grains (see German Patents, 172,851 and 182,099), only one copy being at present attainable.

The screen of the **Paget colour plate** is prepared by giving it a preliminary coating all over with a collodion film dyed red. This is then coated with a resist in such a way that two-thirds of the total area is unprotected, and this is bleached out and dyed green. So that at this stage the plate is covered with a series of red and green lines, the latter being twice the width of the

former. A resist is again applied, but with its lines at right angles to those of the first, and the unprotected portions are bleached and dyed blue. The result is a very transparent and uniform screen firmly attached to the glass. **Omnicolore** and **Dufay** plates are well-known colour plates.

The following are the most important dyes used as sensitisers :—

The Phthaleins.—Of these **erythrosin** and **eosin** are widely used for rendering silver bromide sensitive to yellow and green rays, and consequently for the manufacture of "**Ortho-chromatic**" plates.

Monobromfluorescein is used as a green sensitiser for silver bromide.

Among the **Rosaniline dyes** we may mention that **Ethyl violet** and **Formyl violet** are used as red sensitisers of silver bromide collodion emulsions. **Akridin dyes** are used to some extent as sensitisers for green and blue.

Among the **Azo dyes** used as sensitisers we may mention : **Benzonitrol brown** (By), **Dianil black R** (M., L., & Br.), **Glycin red** (By), **Pluto black** (By), **Wool black 4B** (Agfa). The dyes known as **Alizarin blue bisulphite** and **Nigrosin D** are used to some extent as red sensitisers.

Quinoline Dyes

Are now very important sensitisers (see p. 479). Among them we must mention :—

a. Cyanines

Cyanin (Lepidinquinolineamylcyaniniodide), a blue dye, quite useless for textile purposes on account of its fugitiveness, but used as a sensitiser for silver bromide plates where a panchromatic effect is desired. It renders silver bromide sensitive to red, orange, and yellow rays, with a minimum of sensitiveness between E and F. Its defects are a tendency to fog and speck the plate, accompanied with a diminution in its light-sensitiveness. As a red sensitiser it has been displaced by isocyanines, but it is still used for wet plates and for special kinds of work. Vogel uses a mixture of this dye with quinoline red under the name "Azalin" for sensitising dry plates for green and yellow.

Ethylcyanin (Lepidinquinolinethylcyaninbromide), being more soluble than cyanin, has been proposed as a substitute.

Dicyanin (prepared by action of KOH + atmospheric O on α-γ-Dimethylquinolinium salts) sensitises silver bromide gelatine plates up to the red line *a*, with a strong minimal effect between E and F. Used as a red sensitiser for scientific work, but the prepared plates are not very sensitive.

b. Isocyanines

Of these dyes the most important are :—

Ethyl red, or quinaldinquinolinethylcyanin iodide, which forms green crystals soluble in water and alcohol, with a violet-red colour. In dilute solution (1 : 50,000) it sensitises silver bromide gelatine plates almost uniformly from the red (C) to the violet, with only a small minimum in the green. It does not sensitise far into the red.

Preparations of isocyanines and similar dyes, which are sensitive further in the red, have been put on the market by Meister, Lucius, & Brüning in Höchst-a.-M., under the names **Orthochrom T** (which is *p*-Toluquinaldin-*p*-Toluquinolinethylcyaninbromide), **Pinachrom** (which is *p*-Ethoxyquinaldin-*p*-methoxyquinolineethylcyaninebromide), and **Pinacyanol** (which is obtained by treating quinaldinium salts with formaldehyde, followed by alkali), the latter sensitising in the red up to the B line. **Pinaverdol**, produced by the same firm, is a green sensitiser for silver bromide collodion emulsions, and consists of *p*-Toluquinaldinquinoliniummethylcyaninbromide.

Fr. Bayer in Elberfeld also places several sensitisers on the market. Among these we may mention :—

"**Perikol**," prepared by treating with alcoholic KOH the addition product

obtained from Toluquinaldin and the ethyl ester of Toluene sulphonic acid, sensitises plates to a maximum between $\lambda = 590$ and $\lambda = 560$ $\mu\mu$. "**Isokol**" is a similar preparation. "**Homokol**" is a mixture of quinoline red with an isocyanine dye.

Some of Fr. Bayer's more interesting patents are German Patents, 158,078, 170,048, and 170,049, where the process of manufacture of a number of sensitising dyes are described by acting with alkalis on the addition products of dialkylsulphates with quinaldin and its homologues. The new colouring matters are stated not to fog or fleck plates.

Dyes used for Colour Filters and Similar Purposes

Coloured screens or filters are an absolute necessity in many photographic processes, and a very large number of coal-tar colours are used for the manufacture of these colour filters, which may consist of collodion, gelatine, or aqueous fluids coloured with special dyes which only allow special wave lengths to pass, or which greatly diminish the intensity of the actinic rays.

The screens most widely used consist of glass plates covered with gelatine coloured with a suitable dye.

For developing ordinary dry plates in the dark room the filters used consist of red dyes, and for bromide, yellow dyes. For very fast plates both yellow and red filters are used. For panchromatic and colour-screen plates a faint green light is used.

Auramine O is very suitable, as it absorbs blue and violet, allowing red, green, and yellow rays to pass.

Tartrazin and **Fast Red D** (M., L., & Br.) are good red filters, so also is **Chrysosulphite** (Lumière), which is a mixture of magnesium picrate and sodium sulphite.

Coxin is also a very suitable red filter.

The dyes used for colouring gelatine must be water soluble and free from other adjuncts such as dextrin, Glauber's salt, etc. etc., otherwise the gelatine will not dry clear. The following dyes (among others) are used for colouring the gelatine :—

Auramine, Brilliant green, Crystal violet, Fuchsin, Methylene blue, Phenosafranin, Rhodamin (these also can be used for colouring collodion), also **Acid green, Congo red, Naphthol green, Naphthalene green, Filter yellow, Rapid Filter red, Rapid Filter yellow** (Meister, Lucius, & Brüning), **Patent blue, Tartrazin.**

LIGHT FILTERS

The following light filters are recommended by *Meister, Lucius, & Brüning*, the filters produced being toned for orthochromatic and panchromatic plates :—

Light Filters for the Three-Colour Process

Red Filter.—2.5 g. filter red I. are dissolved in 100 c.c. warm water. 100 c.c. of 8 per cent. gelatine solution are mixed with 4 c.c. of the colour solution and the whole filtered, and 7 c.c. of the gelatine used for every 100 c.c.

Blue Filter.—4 g. crystal violet are dissolved in 100 c.c. warm water and 5-6 drops of acetic acid are added ; then 6 c.c. of coloured solution are added to 100 c.c. of 8 per cent. gelatine solution, and the whole is filtered.

Green Filter.—2.5 g. tartrazine + 6 g. patent blue + 4 g. naphthol green dissolved in 400 c.c. water ; 5 c.c. of colour solution are then added to 100 c.c. of 8 per cent. gelatine solution and the whole filtered.

Time of exposure with orthochromatic plates is blue : green : red :: 1 : 3 : 6.

Light Filters for the Additive Three-Colour Prints

Red Filter.—4 g. tartrazine + 7.5 g. filter red II. in 150 c.c. water. Add 7-8 c.c. of this solution to 100 c.c. of 8 per cent. gelatine solution and filter.

Blue Filter.—3 g. crystal violet + 1 g. methylene blue (free from $ZnCl_2$) + 100 c.c. warm water + 6 drops acetic acid. Add 7-8 c.c. of this coloured solution to 100 c.c. 8 per cent. gelatine solution and filter.

Green Filter.—6 g. tartrazine + 1 g. patent blue + 2 g. naphthol green + 180 c.c. water. 8-9 c.c. of coloured solution is used for 100 c.c. of 8 per cent. gelatine solution.

Times of exposure for orthochromatic plates are blue : green : red = 1 : 5 : 8; for panchromatic plates 1 : 4 : 3.

To make the dry filters 7 c.c. of the coloured gelatines made as above described are poured over every 100 sq. cm. of plate surface and allowed to set; then two coloured plates are taken together and fixed with Canada balsam.

In the three-colour photographic process such dyes as **Aurophenin** or **Naphthol yellow S, Erythrosin, Diamine pure blue** or **Fast bluish green** are used to colour the partial pictures.

FLASHLIGHTS

Powdered magnesium was introduced as a flashlight in 1887. Since then many other flashlights have been introduced—usually by mixing the magnesium with an oxygen-rich substance. Many of these preparations are very explosive, and must not be blown into a flame. We may notice the following recipes:—

1. 2 parts Mg powder + 3 parts powdered potassium permanganate.

2. 15 parts Mg powder + 30 parts $KClO_3$ + 5 parts antimony sulphide, finely powdered and mixed dry. Explosive, so must not use a mortar.

3. Smokeless flashlight mixtures giving an intense light consist of magnesium or aluminium powder + nitrates of rare earths (thorium, zirconium). See German Patent, 158,215; see also English Patent, 27,267 (1904), where rare earths are added to Mg or Al flashlights. Fr. Bayer & Co. (German Patent, 136,313) place a number of excellent flashlights on the market; they appear to consist of Mg + manganese peroxide, to which are added bodies like $Sr(NO_3)_2$, which yield a coloured flame. See also English Patent, 27,466, 1904. Such mixtures are termed ortho- or panchromatic flashlights, since they give out orange rays in addition to the blue or violet rays emitted by the ordinary mixture. Other proposed mixtures are: of Mg powder + silica + boric acid (German Patent, 101,528); Al powder + $KClO_3$ (German Patent, 101,735); Mg powder + red phosphorus + peroxides. Very powerful photo effects are obtained by adding cadmium nitrate in quantity equal to magnesium powder. Zinc nitrate also is used.

Time Lights do not flash, but burn slowly, an effect attained by adding to magnesium (sometimes mixed with aluminium) powder bodies such as carbonates, silicates, or oxides of the alkaline earths—*e.g.*, $SrCO_3$. Bayer (German Patent, 165,259) proposes Mg or Al powder + Na_2WO_4, or WO_3, as a smokeless time light. Novak proposes Mg powder + cerium nitrate + $SrCO_3$ as a smokeless time light.

Kreb's panchromatic time lights give out coloured rays, thus enabling the taking of photographs of objects by colour sensitive plates without the use of a yellow light filter. Electric metallic filament lamps are also used now.

DEVELOPERS

We can give here only a brief mention of some of the more important reducing substances used in the manufacture of developers.

Iron Oxalate is one of the oldest developers, and is still used to some extent—usually in the form of two solutions, I. and II., I. consisting of 300 g. neutralised potassium oxalate in 1,000 c.c. of water, and II. of ferrous sulphate solution (100 g. $FeSO_4$ + 300 c.c. water + 5 drops concentrated H_2SO_4). For use, 3-4 parts of I. are used with 1 of II.

Developers derived from Monohydric Phenols

Paramidophenol, $C_6H_4\begin{matrix}OH\\NH_2\end{matrix}$ (1 : 4), produced by reducing *p*-nitrophenol with tin + HCl.* Colourless crystals, M.P. 184°; forms a crystalline hydrochloride, $OH.C_6H_4.NH_2.HCl$.

"Rodinal" contains *p*-amidophenolhydrochloride. "Unal" is rodinal in a solid form.

Monomethylparamidophenol, $C_6H_4(OH)(NHCH_3)$, 1 : 4, is prepared by methylating *p*-amidophenol.

It is an excellent developer, giving results free from stain. It is known as "scalol." Two solutions are used: (A) "Scalol," 1.5 g. + hydro-quinone, 3 g. + sod. sulphite (crystals), 28 g. + KBr, 0.25 g. + H_2O, 284 c.c.; (B) Na_2CO_3 (crystals), 30 g. + H_2O, 300 c.c. Use equal parts of A and B.

"Metol" is the sulphate of this body. The developer "Satrapol" also contains it. Metol works exceedingly rapidly. Stock solution: 15 g. metol + 150 g. cryst. sod. sulphite + 75 g. K_2CO_3 + 2 g. KBr + 1,000 c.c. H_2O.

"Metolhydroquinone" developer, now widely used, consists of the two solutions: (A) 2 g. metol + 3.5 g. hydroquinone + 4 g. Na_2HPO_4 + 400 c.c. H_2O + 2 c.c. sodium sulphite solution (1 : 100). (B) 40 g. K_2CO_3 + 400 c.c. H_2O. For use mix equal parts of A and B.

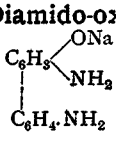
Diamidophenol, $C_6H_3(OH)(NH_2)(NH_2)$, 1 : 2 : 4, is prepared by reducing with Sn + HCl 1 : 2 : 4-dinitrophenol; forms salts with HCl and H_2SO_4.

"Amidol" consists of 20 g. diamidophenol sulphate or chloride + 200 g. cryst. sod. sulphite + 1,000 c.c. H_2O. Solution will not keep. Best developer for bromides and gaslight papers. Valenta proposes acetonesulphite + diamidophenol hydrochloride as a powerful developer.

***p*-Amido-saligenin**, $C_6H_3(CH_2OH)(OH)(NH_2)$, 1 : 2 : 3, in the form of its hydrochloride, occurs as an easily soluble white powder, similar in properties to amidol, but having the advantage of allowing very concentrated solutions being formed.

"Edinol" (made by Fr. Bayer, Elberfeld) consists of 5 g. *p*-amido-saligenin + 7.5 g. acetone sulphite + 30 g. KOH + 0.5 g. KBr + 100 c.c. H_2O. Edinol-hydroquinone developer consists of 2 g. *p*-amido-saligenin + 1 g. hydroquinone + 5 g. acetone sulphite + 30 g. cryst. sod. sulphite + 30 g. K_2CO_3 + 150 c.c. H_2O.

Diamido-oxydiphenyl, in the form of its sodium salt, is used in a manner similar to "Rodinal." Placed on the market under the name "Diphenal" by Cassella & Co.



***p*-Oxyphenylglycocoll**, $C_6H_4(OH)(NH.CH_2.CO_2H)$, 1 : 4, is manufactured by heating *p*-amidophenol, $C_6H_4(OH)(NH_2)$, with monochloracetic acid, $CH_2Cl.COOH$, in aqueous solution.

Used as a developer, it gives pure black tones and keeps well. It is placed on the market as "Glycin." Stock solutions are: 5 g. glycin + 25 g. cryst. sod. sulphite + 100 c.c. H_2O + 25 g. K_2CO_3 Another good keeping solution is 2 g. glycine + 800 c.c. H_2O (recently boiled) + 2 g. cryst. sod. sulphite + 15 g. K_2CO_3. It is used chiefly for stand development because it does not produce chemical fog by long action.

Methylorthoamidophenol, $C_6H_4(OH)(NHCH_3)$, 1 : 2, 2 molecules of which, combined with 1 molecule of hydroquinone, forms the basis of the excellent developer "Ortol."

Two naphthalene compounds are used as developers :—

Sodium α_1-amido-β_1-naphthol-β_3-sulphonate, $C_{10}H_5(OH)(NH_2)(SO_3Na)$, a good developer if used at 20° C. or a little below. It forms the basis of Eikonogen. One of the best developers for plates which have received very short exposure.

Hydroquinone-eikonogen developer consists of two solutions, A and B: (A) 100 g. cryst. sod. sulphite + 16 g. eikonogen + 4 g. hydroquinone + 900 c.c. boiling water; (B) 40 g. K_2CO_3 + 200 c.c. H_2O. For use, 40 c.c. of A are added to 180 c.c. B, together with 3 drops 10 per cent. KBr solution.

Sodium amidonaphtholdisulphonate, $C_{10}H_4(NH_2)(OH)(SO_3Na)_2$, which forms the basis of the developer "Diogen."

Developers derived from Dihydric Phenols

Hydroquinone, $C_6H_4(OH)_2$, 1 : 4, is a developer much used by amateurs, giving strong hard negatives of a bluish black tone.

The best preparation occurs as yellowish crystals, and is obtained by recrystallising the commercial product in the presence of SO_2. The stock solution consists of 5 g. hydroquinone + 40 g. cryst. sod. sulphite + 6.5 g. KOH + 150 c.c. H_2O. It is frequently combined with other developers. See **Edinol, Eikonogen, Metol.**

Monochlor and Monobromhydroquinones, $C_6H_3Cl(OH)_2$ and $C_6H_3Br(OH)_2$, are now used as developers under the name "**Adurol**" (see German Patent, 111,798).

Monochlorhydroquinone is obtained by leading Cl gas through hydroquinone dissolved in benzol, while the bromo derivative is obtained by adding a solution of Br in benzol to a hydroquinone benzol solution, evaporating the benzol and crystallising from ligroin.

"Adurol" developer consists of the stock solutions: (A) 10 g. adurol + 80 g. cryst. sod. sulphite + 500 c.c. H_2O; (B) 60 g. K_2CO_3 + 500 c.c. H_2O. One part A, one part B, and one part H_2O are taken to develop. Adurol comes between hydroquinone and the "rapid developers" (metol, rodinal, etc.) in properties. It does not turn brown by oxidisation in air, and so may be repeatedly used.

Pyrocatechol, $C_6H_4(OH)_2$, 1 : 2, has been proposed as a developer, and under the name "Kachin" has been placed on the market.

Resorcin, $C_6H_4(OH)_2$, 1 : 3, is of no use as a developer. Two amido derivatives of it, however, are used for this purpose, namely, **Diamidoresorcin**, $C_6H_2{}^{(4:6)}(NH_2)_2{}^{(1:3)}(OH)_2$, and **Triamidoresorcin**, $C_6H(NH_2)_3(OH)_2$ ("Reducin").

Developers derived from Trihydric Phenols

Pyrogallol, $C_6H_3(OH)_3$ (1 : 2 : 3), is the basis of most of these. Pyrogallol developers work rapidly, but have the drawback that they stain the fingers, are poisonous, and do not keep well.

Pyrosoda Developer.—Stock solutions: (A) 10 g. pot. metabisulphite + 83 g. pyrogallol + 13 g. KBr + water up to 1,000 c.c.; (B) 100 g. Na_2SO_3 + 100 g. Na_2CO_3 + H_2O up to 1,000 c.c. For use mix 1 part A with 1 part B and 1 part H_2O.

Pyropotash Developer.—Stock solutions: (A) 25 g. cryst. Na_2SO_3 + 100 c.c. H_2O + 10 g. pyrogallol + 3-4 drops H_2SO_4; (B) 45 g. K_2CO_3 + 12.5 g. Na_2SO_3 in 100 H_2O. Use 3 c.c. A and 3 c.c. B with 100 c.c. H_2O.

Pyrometol.—Stock solutions: (A) 5 g. metol + 14 g. pot. metabisulphite + 6 g. pyrogallol + 2 g. KBr + H_2O up to 1,000 c.c.; (B) 200 g. Na_2CO_3 + 1,000 c.c. H_2O. Use equal quantities of A and B. Gives a good printing yellow negative.

"**Pinakol P**" is an excellent developer made by replacing in the pyropotash developer the alkali by half the equivalent amount of **sodium amidoacetate**, $CH_2NH_2.COONa$. Developing with "Pinakol P" gives stronger, clearer, and more rapid results than the old pyro developers; moreover, it does not stain the fingers.

Pinakol Salt N is a 20 per cent. solution sodium amidoacetate, $CH_2NH_2.COONa$. It is used for replacing alkali in organic developers since it does not affect the skin of the operator and the gelatine film in the unpleasant way that alkali does; moreover the results attained are superior to those of soda and potash.

Acetone bisulphite, acetone-sulphite "Bayer," is now largely used as a substitute for sodium or potassium bisulphite in developers. It is antiseptic, a restrainer for rapid developers, a clearing agent for fixing baths and developing papers, and is used also for darkening the negative after the use of mercury intensifiers.

FIXING, TONING, AND COMBINED BATHS

Sodium Thiosulphate, $Na_2S_2O_3 + 5H_2O$, is now practically the only fixing salt used. The fixing occurs according to the equation:—

$$2AgBr + Na_2S_2O_3 = Ag_2S_2O_3 + 2NaBr;$$

the $Ag_2S_2O_3$ then combines with the excess of $Na_2S_2O_3$ to form the soluble double salt $Ag_2S_2O_3.2Na_2S_2O_3$.

The thiosulphate may be used in neutral solution (1 : 4 H_2O) but is best used in acid bisulphite fixing solution, and sometimes alum is added (to harden the gelatine).

The following are well-known gold **toning** baths:—

Ordinary Toning Bath.—(A) 4 g. borax in 1,000 c.c. H_2O; (B) 4.5 g. anhydrous sodium acetate in 1,000 c.c. H_2O; (C) 1 g. gold chloride in 50 c.c. H_2O. Use 8-10 c.c. of C + 100 c.c. A + 100 c.c. B.

Neutral Toning and Fixing Bath.—250 g. sodium thiosulphate + 20 g. lead acetate + 10 g. calcium chloride + 0.4 g. gold chloride + 1,000 c.c. H_2O.

Acid Toning and Fixing Bath.—250 g. sodium thiosulphate + 25 g. ammonium sulphocyanide + 10 g. lead acetate + 5 g. citric acid + 0.4 g. gold chloride + 1,000 c.c. H_2O.

Platinum toning baths are also used, the basis being $PtCl_4$ or $PtCl_2$, which reacts with Ag salts thus: $4Ag + PtCl_4 = 4AgCl + Pt$.

Palladium Chloride, used as a toning bath for silver pictures, gives beautiful brown tones.

Sodium Thiosulphate Destroyers.—A lengthy washing is required to remove the last traces of sodium thiosulphate, and the durability of the print largely depends on its complete removal. Consequently attempts have been made to find substances which rapidly destroy the last traces of thiosulphate. The best known substances are **Anthion** = potassium persulphate, **Thioxydant Lumière** = ammonium persulphate. More recently **percarbonates, perborates,** and **permanganates** have been suggested.

Bayer's "Hypo-destroyer" = persulphate + percarbonate. "Antihypo" is potassium percarbonate. 10 g. are dissolved in 1,000 c.c. H_2O and the plates and paper, after rinsing, are immersed for a few minutes after which only a short rinsing is necessary. A great time-saving is thus effected.

REDUCERS AND INTENSIFIERS

Reducers are chemicals which act by dissolving the fine silver particles. A large number of such substances are known, being oxygen-rich substances such as chromic acid, mercuric nitrate, ferric-, manganic-, ceric-, and titanic-salts, persulphates, etc.

Farmer's reducer = 100 c.c. sodium thiosulphate solution 1 : 4 + 8 c.c. of a 10 per cent. potassium ferricyanide solution. This destroys the fine middle tones, and so increases the contrasts. **Ammonium persulphate reducers** diminish the contrasts by acting on the darker parts of the plate. **Cerium sulphate** makes a very uniform reducer.

Intensifiers are used to increase the density of thin negatives, and bring out the contrasts better. The **mercury intensifying process** consists in treating the negative with a solution containing 2 per cent. mercuric chloride + 2 per cent. KBr. When the negative is grey it is removed, rinsed, and immersed in a 12 per cent. solution of sodium sulphite, when the negative becomes black again: $2Ag + 2HgCl_2 = 2HgAgCl_2$, then

$$4AgHgCl_2 + 7Na_2SO_3 + xNa_2SO_3 = Ag_2 + Hg + Ag_2SO_3.xNa_2SO_3 + 3HgNa_2(SO_3)_2 + 8NaCl.$$

The **uranium** intensifying process requires two solutions: (A) 1 g. uranium nitrate + 100 c.c. H_2O; (B) 1 g. potassium ferricyanide + 100 c.c. H_2O. For use, 50 c.c. A + 11 c.c. acetic acid + 50 c.c. of B are mixed. Other intensifying solutions used are: $CuSO_4$ + pot. ferricyanide + pot. citrate, and $HgI_2 + Na_2SO_3$. Intensifiers containing **bichromate** are also used.

PHOTOGRAPHIC PAPERS

An enormous number of these exist: we may class them into—

1. **Printing-out Papers.** — The p.o.p. papers are still made (although developing papers are said to be rapidly supplanting them) and usually employ silver chloride as the sensitive substance. Four well-defined groups of papers are manufactured: (*a*) **Albumen papers** in which the ground is albumen and the sensitive substance silver chloride. (*b*) **Silver chloride gelatine paper;** here the ground is gelatine and the sensitive substance silver chloride. (*c*) **Silver chloride collodion papers.** (*d*) **Silver chloride casein papers** give good results and resist high temperatures. Direct printing platinum papers are also on the market.

On exposure to light the chloride is converted to a "photo-chloride," Ag_2Cl, of a purple or reddish colour, and stated to be an adsorption compound of silver chloride and silver, of variable composition. After the paper has been printed the colour of the deposit is modified by immersion in a bath containing a gold or platinum salt, associated with a weak reducer, so that metallic gold or platinum is precipitated ("Toning"). The unused silver chloride, AgCl, is then dissolved out by thiosulphate ("Fixing"), which only slightly attacks the photo-chloride.

2. **Developing Papers.**—These may also be grouped into five classes, namely: (*a*) **Silver bromide papers** consisting of an emulsion of silver bromide + gelatine; used for printing and enlargements; very sensitive and must be worked in a dark room. (*b*) **Silver chlorobromide papers** can be used for printing in ordinary shaded daylight or by gaslight. (*c*) **Silver phosphate papers** may be printed in weak daylight or by gaslight. When developed they give p.o.p. effects. (*d*) **Platinum** developing papers give excellent results. (*e*) **Pigment papers** are covered with chromgelatine, which under the influence of light becomes insoluble in hot water. As any pigment can be mixed with the gelatine very beautiful

coloured results are obtainable. In the bromoil process the bleached bromide print is worked up with special inks.

The chief difference between emulsions for development papers and those for plates is that paper emulsions are of a much lower sensitiveness (finer grain), and contain a larger proportion of silver to gelatine, the coating being thin so as to keep the image on the surface of the paper. The colour of the image obtained depends upon the size of the grain, and developers can be used by which the silver is deposited in a very finely divided state, almost approaching to colloidal solution. By the admixture of such fine grain silver with larger grains, various tones can be obtained upon development. The papers, which are sometimes faced with $BaSO_4$, are manufactured by passing through a trough containing the emulsion, then over a cold roller to set the gelatine, then hung up in loops in a long drying chamber, through which it slowly travels, emerging dry after about two and a half hours. It is then rolled direct and cut. Surface-coated papers without gelatine, such as platinum papers, are dried almost instantly on a short machine by hot air, and do not require the elaborate hanging and slow drying arrangements used for gelatine-coated papers.

Acknowledgment.—My best thanks are due to Mr S. Allen for expert advice and many suggestions. He kindly revised the proof sheets of the above article.

APPENDIX I

TABLE I

WEIGHTS AND MEASURES

1. METRIC SYSTEM

1 metre (m.) = 10 decimetres (dm.) = 100 centimetres (cm.) = 1,000 millimetres (mm.) = 1.09 yards = 3.281 feet = 39.371 inches.

1 litre (l.) = 1,000 cubic centimetres (c.c. or c.cm.) = 0.22 gallon = 1.76 pints = 35.2 fluid oz.

1 cubic metre (cb.m.) = 1,000 litres = 220 gallons.

1 gramme (g. or gr. or grm.) = 10 decigrammes (dg.) = 100 centigrammes (cg.) = 1,000 milligrammes (mg.) = 15.43 grains.

1,000,000 grammes = 1 metric ton; 1,017,960 grammes = 1 ton of 2,240 lbs.

1 kilogramme (Kg. or Kilo.) = 1,000 grammes = 35.27 oz. = 2.2 lbs.

50 kilogrammes = 1 centner = 1 cwt., nearly.

100 kilogrammes = 1 quintal or 1 metric centner = 1 doppelzentner = 1 dz. = about $\frac{1}{10}$th ton.

1,000 kilogrammes = 1 ton (t.), *i.e.*, *metric ton* = 19 cwt. 77 lbs. = 2204.6 lbs.

1 cubic centimetre water = 1 gramme.

1 litre water = 1 kilogramme = 2.2 lbs.

1 cubic metre water = 1 metric ton = 2204.6 lbs.

2. ENGLISH WEIGHTS AND MEASURES

1 yard (yd.) = 3 feet = 91.44 centimetres = 0.9144 metre.

1 foot (′) = 12 inches (″) = 30.48 centimetres = 0.3048 metre; 1 cubic foot = 28.315 litres.

1 inch = 2.54 centimetres; 1 cubic inch = 0.01639 litre.

1 imperial gallon (gal.) = 4 quarts (qts.) = 8 pints (pts.) = 16 gills = 32 noggins = 10 lbs. (of water) = 4.54 litres.

1 pint = 0.568 litre = 2 gills = 4 noggins = 1¼ lbs. (water).

In England, by the term gallon (gal.) the Imperial gallon is meant, but in the United States of America the much smaller *apothecary's* or *wine gallon* is understood.

1 imperial gallon = 1.2 wine gallons; 1 wine gallon = 0.8335 imperial gallon.

1 wine gallon = 4 quarts = 8 pints = 3.785 litres = 8.35 lbs. water; 1 litre = 0.264 wine gallon.

1 pint (apothecary's measure) = 0.473 litre; 1 litre = 0.264 pint (apothecary's measure).

1 pound avoirdupois (lb.) = 16 oz. = 256 drachms (drm.) = 7,000 grains = 453.6 grams = 0.454 Kilo.

1 oz. = 16 drachms = 437.5 grains = 28.35 grams; 1 fluid oz. = 28.4 c c.

1 hundredweight = 4 quarters (28 lbs. each) = 112 lbs.

1 ton (gross ton) = 20 cwt. = 2,240 lbs. = 1,016 Kilos. = 1.016 metric tons.

In England the ton or gross ton of 2,240 lbs. is exclusively used. In the United States of America the term "ton" may mean the gross ton of 2,240 lbs., or the short ton of 2,000 lbs. avoirdupois.

1 grain = 0.0648 gram; 7,000 grains = 1 lb.

TABLE II

COMPARISON OF THERMOMETERS—CONVERSION OF THERMOMETER DEGREES

° C. to ° F.: multiply by 9, divide by 5, then add 32.
° F. to ° C.: first subtract 32, then multiply by 5, and divide by 9.

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES

° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.
+500	+932	+74	+165.2	+45	+113	+16	+60.8
400	752	73	163.4	44	111.2	15	59
300	572	72	161.6	43	109.4	14	57.2
200	392	71	159.8	42	107.6	13	55.4
100	212	70	158	41	105.8	12	53.6
99	210.2	69	156.2	40	104	11	51.8
98	208.4	68	154.4	39	102.2	10	50
97	206.6	67	152.6	38	100.4	9	48.2
96	204.8	66	150.8	37	98.6	8	46.4
95	203	65	149	36	96.8	7	44.6
94	201.2	64	147.2	35	95	6	42.8
93	199.4	63	145.4	34	93.2	5	41
92	197.6	62	143.6	33	91.4	4	39.2
91	195.8	61	141.8	32	89.6	3	37.4
90	194	60	140	31	87.8	2	35.6
89	192.2	59	138.2	30	86	1	33.8
88	190.4	58	136.4	29	84.2	0	32
87	188.6	57	134.6	28	82.4	-1	30.2
86	186.8	56	132.8	27	80.6	2	28.4
85	185	55	131	26	78.8	3	26.6
84	183.2	54	129.2	25	77	4	24.8
83	181.4	53	127.4	24	75.2	5	23
82	179.6	52	125.6	23	73.4	6	21.2
81	177.8	51	123.8	22	71.6	7	19.4
80	176	50	122	21	69.8	8	17.6
79	174.2	49	120.2	20	68	9	15.8
78	172.4	48	118.4	19	66.2	10	14
77	170.6	47	116.6	18	64.4	11	12.2
76	168.8	46	114.8	17	62.6	12	10.4
75	167						

TABLE III

COMPARISON OF HYDROMETER DEGREES TWADDLE AND BAUMÉ WITH THE SPECIFIC GRAVITIES FOR LIQUIDS HEAVIER THAN WATER

Degrees Twaddle.	Degrees Baumé.	Specific Gravity.	Degrees Twaddle.	Degrees Baumé.	Specific Gravity.	Degrees Twaddle.	Degrees. Baumé.	Specific Gravity.
1	0.7	1.005	64	35.0	1.320	128	56.3	1.640
2	1.4	1.010	66	35.8	1.330	130	56.9	1.650
4	2.7	1.020	68	36.6	1.340	132	57.4	1.660
6	4.1	1.030	70	37.4	1.350	134	57.9	1.670
8	5.4	1.040	72	38.2	1.360	136	58.4	1.680
10	6.7	1.050	74	39.0	1.370	138	58.9	1.690
12	8.0	1.060	76	39.8	1.380	140	59.5	1.700
14	9.4	1.070	78	40.5	1.390	142	59.9	1.710
16	10.6	1.080	80	41.2	1.400	144	60.4	1.720
18	11.9	1.090	82	42.0	1.410	146	60.9	1.730
20	13.0	1.100	84	42.7	1.420	148	61.4	1.740
22	14.2	1.110	86	43.4	1.430	150	61.8	1.750
24	15.4	1.120	88	44.1	1.440	152	62.3	1.760
26	16.5	1.130	90	44.8	1.450	154	62.8	1.770
28	17.7	1.140	92	45.4	1.460	156	63.2	1.780
30	18.8	1.150	94	46.1	1.470	158	63.7	1.790
32	19.8	1.160	96	46.8	1.480	160	64.2	1.800
34	20.9	1.170	98	47.4	1.490	162	64.6	1.810
36	22.0	1.180	100	48.1	1.500	164	65.0	1.820
38	23.0	1.190	102	48.7	1.510	166	65.5	1.830
40	24.0	1.200	104	49.4	1.520	168	65.9	1.840
42	25.0	1.210	106	50.0	1.530	169	66.1	1.845
44	26.0	1.220	108	50.6	1.540	170	66.3	1.850
46	26.9	1.230	110	51.2	1.550		67	1.872
48	27.9	1.240	112	51.8	1.560		68	1.897
50	28.8	1.250	114	52.4	1.570		69	1.921
52	29.7	1.260	116	53.0	1.580		70	1.946
54	30.6	1.270	118	53.6	1.590		71	1.974
56	31.5	1.280	120	54.1	1.600		72	2.000
58	32.4	1.290	122	54.7	1.610		73	2.031
60	33.3	1.300	124	55.2	1.620		74	2.059
62	34.2	1.310	126	55.8	1.630			

Note.—The degrees in Twaddle's hydrometer bear a direct relationship to the specific gravity and may be obtained from the same by the following formula in which d represents the specific gravity and n the number of degrees Twaddle: $n = \frac{1000\,d - 1000}{5}$. On the other hand by the formula $d = \frac{5n + 1000}{1000}$ the degrees Twaddle are converted into the corresponding specific gravity. For values below 2.0 the degrees Twaddle may also be obtained from the specific gravity by moving the decimal point two figures to the right, striking off the first figure and multiplying the rest by 2, as per the following example:—

Specific gravity 1.133:
113.3:
13.3 × 2:
26.6° Twaddle.

TABLE IV

DENSITIES CORRESPONDING TO BAUMÉ'S HYDROMETER FOR LIQUIDS LIGHTER THAN WATER (*Francœur*)

° B.	Density.	° B.	Density.	° B.	Density.	° B.	Density.
10	1.000	23	0.918	36	0.849	49	0.789
11	0.993	24	0.913	37	0.844	50	0.785
12	0.986	25	0.907	38	0.839	51	0.781
13	0.980	26	0.901	39	0.834	52	0.777
14	0.973	27	0.896	40	0.830	53	0.773
15	0.967	28	0.890	41	0.825	54	0.768
16	0.960	29	0.885	42	0.820	55	0.764
17	0.954	30	0.880	43	0.816	56	0.760
18	0.948	31	0.874	44	0.811	57	0.757
19	0.942	32	0.869	45	0.807	58	0.753
20	0.936	33	0.864	46	0.802	59	0.749
21	0.930	34	0.859	47	0.798	60	0.745
22	0.924	35	0.854	48	0.794		

APPENDIX II.

INDEX LIST OF TRADE NAMES OF THE NEWER SYNTHETIC DRUGS. PHOTOGRAPHIC DEVELOPERS, ETC.

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Abanone.—Magnesium phosphotartrate.

Acetomorphine.—Diacetylmorphine, $C_{17}H_{17}NO_3(C_2H_3O)_2$.

Acetopyrin.—Antipyrine acetylsalicylate, $C_{11}H_{12}N_2O,C_2H_3O.OC_6H_4.COOH$.

Acetosal.—Acetylsalicylic acid, $C_2H_3O.OC_6H_4.CO_2H$.

Acetozone.—Mixture of equal parts of acetylbenzoyl peroxide, $C_6H_5CO.O.O.C_2H_3O$, and kieselguhr.

Acetysal. See acetosal.

Acidol.—Betaine hydrochloride, $C_5H_{11}NO_2,HCl$.

Acitrin.—2-Phenylquinoline-4-carboxylic acid ethyl ester, $C_9H_5N(C_6H_5)CO_2C_2H_5$.

Acopyrin. See acetopyrin.

Adalin.—Bromodiethylacetylurea, $(C_2H_5)_2CBr.CO.NH.CO.NH_2$.

Adamon.—Dibromodihydrocinnamic acid bornyl ester, $C_6H_5(CHBr)_2CO_2C_{10}H_{17}$.

Adigan.—Digitalis preparation containing all the active principles except digitonin, this having been removed by precipitation with cholesterol in alcoholic solution.

Adrenal.—Crystalline base from the suprarenal gland.

Adrenaline.—*o*-Dihydroxyphenylmethylaminomethylcarbinol hydrochloride, $(HO)_2C_6H_3.CH(OH).CH_2.NH(CH_3),HCl$.

Adreucaine. See eudrenine.

Afridol.—Sodium salt of hydroxymercury-*o*-toluic acid, $CH_3.C_6H_3(CO_2Na)HgOH$.

Agnin.—Adeps lanæ or purified wool fat.

Agnolin. See agnin.

Agobilin.—Strontium cholate mixed with small quantities of strontium salicylate and diacetylphenolphthalein.

Agurin.—Addition product of theobromine-sodium and sodium acetate, $C_7H_7N_4O_2Na,C_2H_3O_2Na$.

Albargin.—Gelatose-silver (15 % Ag).

Aldoform.—A formaldehyde preparation.

Aleudrin.—Carbamic acid ester of *aa*-dichloroisopropyl alcohol, $(CH_2Cl)_2.CH.O.CO.NH_2$.

Alformin.—16 % solution of basic aluminium formate, $Al_2(OH)_2(HCO_2)_4$.

Alginoid iron. See algiron.

Algiron.—Iron compound of alginic acid (from seaweed); contains 11 % Fe.

Allmatein.—Condensation product of hæmatoxylin and formaldehyde, $CH_2O_2(C_{16}H_{12}O_6)_2 : CH_2$

Allosan.—Santalyl allophanate, $NH_2.CO.NH.CO_2.C_{15}H_{23}$.

Alphogen.—Succinyl peroxide, $(COOH.CH_2.CH_2.CO)_2O_2$.

Alphozone. See alphogen.

Althein.—Asparagin, $C_2H_3(NH_2)(CO_2H)CO.NH_2 + H_2O$.

Alypin.—Benzoyl-1.3-tetramethyldiaminoethyl 2-isopropyl alcohol hydrochloride, $C_6H_5CO.O(C_2H_5)C[CH_2.N(CH_3)_2]_2,HCl$.

Amarin.—Triphenyldihydroglyoxaline,

$$C_6H_5.C.NH\rangle CH.C_6H_5.$$
$$C_6H_5.C.NH$$

Amenyl.—Methylhexamethylenetetramine hydrochloride, $CH_2O_2 : C_6H_{12}(CO)_2N(CH_3),HCl$.

Amidopyrin.—Dimethylamineantipyrine, $C_{11}H_{11}N_2O.N(CH_3)_2$.

Amphotropin.—Hexamethylenetetramine camphorate, $(C_6H_{12}N_4)_2,C_8H_{14}(COOH)_2$.

Amylarine.—Isoamyltrimethylammonium hydroxide, $C_5H_{11}(CH_3)_3N.OH$.

Anæsthesin.—Ethyl ester of *p*-aminobenzoic acid, $NH_2.C_6H_4.CO_2C_2H_5$.

Anæsthone. See anæsthesin.

Analutos. See kalmopyrin.

Angioneurosin.—Nitroglycerin, $C_3H_5(O.NO_2)_3$.

Anisotheobromine.—Addition product of theobromine-sodium and sodium anisate, $C_7H_7N_4O_2Na,C_8H_4(OCH_3)CO_2Na$.

Anogon.—Mercury salt of 2.6-di-iodophenol-4-sulphonic acid, $C_6H_2I_2(OHg)(SO_3Hg)$.

Antacedin.—Calcium saccharate.

Anthrasol.—Coal tar distillate having colour and consistence of olive oil.

Antiarthrin.—Condensation product of saligenin and tannin, probably the hydroxybenzyl ester of tannic acid.

Antileprol.—Purified chaulmoogra oil.

Antiluetin.—Potassium-ammonium antimonyltartrate, $[SbO(C_4H_4O_6)_2KNH_4]_2H_2O$.

Antiperiostin.—Mercury iodocantharidate, $C_8H_{11}IO(COO)_2Hg$.

Antipyoninum.—"Neutral" sodium tetraborate, prepared by fusing together borax and boric acid.

Antisclerosine.—Mixed inorganic salts of normal blood.

Antodin.—Phenyl ether of glycerol, $C_3H_5(OH)_2O.C_6H_5$.

Aperitol.—Mixture of equal parts of isovaleryl- and acetyl-phenolphthalein.

Aponal.—Amyl carbamate, $NH_2.COOC_5H_{11}$.

Appallagin.—Mercury compound of nosophen (tetraiodophenolphthalein).

Apyron.—Lithium acetylsalicylate, $C_2H_3O.OC_6H_4.CO_2Li$.

Archibromin.—Monobromoisovalerylglycolylurea. $CH_2(OH).CO.NH.CO.NH.CO.C_4H_8Br$.

Archiodin.—Monoiodoisovalery lglycolylurea.

Argaldin.—Combination of albumin-silver and hexamethylenetetramine (10 % Ag).

Argoferment—Colloidal silver.

Argyrol.—Silver-vitellin (20-30 % Ag).

Argulan.—Mercury compound of dimethylphenyl-pyrazolonesulphamine, $C_{11}H_{11}N_2O.NH.SO_3HgOH$.

Arheol.—Santalol, $C_{15}H_{24}O$.

Arhoin.—Addition product of diphenylamine and ethylthymyl-benzoate, $(C_6H_5)_2NH,C_{10}H_{13}.C_6H_4.CO_2C_2H_5$.

Aristochin. See aristoquinine.

Aristoquinine.—Carbonic ester of quinine, $CO(OC_{20}H_{23}N_2O)_2$.

Arrhenal.—Sodium methylarsinate, $AsO(CH_3)(ONa)_2,6H_2O$.

Arsacetin.—Sodium *p*-acetylaminophenylarsinate, $C_2H_3O.NH.C_6H_4AsO(ONa)(OH),3\text{-}4H_2O$.

Arsacetin-quinine.—Contains 43 % of arsacetin and 54 % of quinine.

Arsalyt.—Bismethylaminotetra-aminoarsenobenzene.

Arsamin. See atoxyl.

Arsan.—Glidin preparation containing silver.

Arsanilic Acid.—*p*-Aminophenylarsinic acid, $NH_2.C_6H_4AsO(OH)_2$.

Arsen-phenol-amine. See salvarsan.

Arterenol.—*o*-Dihydroxyphenylaminomethylcarbinol hydrochloride, $(HO)_2C_6H_3.CH(OH).CH_2NH_2,HCl$.

Asiphyl. See asyphil.

Aspirin, Soluble. See kalmopyrin.

Aspirophen.—Aminoacetphenetidide acetylsalicylate, $C_2H_5O.C_6H_4.NH.C_2H_2O.NH_2,C_2H_3O.OC_6H_4.COOH$.

Asquirrol.—Mercury dimethoxide, $(CH_3O)_2Hg$.

Astrolin.—Antipyrine methyl-ethyl-glycollate.

Asurol.—Addition product of mercury salicylate and sodium aminohydroxy-isobutyrate.

Asyphil.—Mercury salt of atoxyl, $(NH_2C_6H_4.AsO.(OH)O)_2Hg$.

Atophan.—2-Phenylquinoline-4-carboxylic acid, $C_9H_5N(C_6H_5)COOH$.

Atoxyl.—Sodium *p*-aminophenylarsinate, $NH_2.C_6H_4.AsO(OH)(ONa),xH_2O$.

Atrinal.—Atropinesulphuric acid, $C_{17}H_{25}O_6NS$.

Atyrosyl. See asyphil.

Azovernin.—Acetylaminoazotoluene, $CH_3.C_6H_4.N_2.C_6H_3(CH_3).NH.C_2H_3O$.

Barbitone. See veronal.

Barutin.—Addition product of theobromine-barium and sodium salicylate.

Benzinoform.—Carbon tetrachloride.

Benzosalin.—Methyl benzoyl salicylate, $C_6H_4(O.CO.C_6H_5)COOCH_3$.

Biogen.—Magnesium peroxide.

Biolactyl.—Preparation of lactic acid bacilli.

Biseiniod.—Combination of cinchonidine hydriodide and bismuth iodide, $C_{19}H_{22}N_2O,HI,BiI_3$.

Bismon.—Colloidal bismuth.

Bismutose.—Contains about 22 % Bi and 66 % albumin.

Blankit.—Sodium hydrosulphite.

Blenal.—Carbonic acid ester of santalol, $CO(OC_{15}H_{23})_2$.

Bornyval.—Bornyl isovalerate, $C_4H_9CO.O.C_{19}H_{17}$.

Bornyval, New.—Bornyl isovaleryl glycollate, $C_4H_9COOCH_2.COOC_{10}H_{17}$.

Boroform.—Solution of formaldehyde in sodium glyceroborate.

Borsalyl.—Sodium borosalicylate.

Borovertin.—Hexamethylenetetramine triborate, $C_6H_{12}N_4,3HBO_2$.

Bromeigon.—Albumin preparation containing bromine.

Bromelia, cryst.—*β*-Naphthyl ethyl ether, $C_{10}H_7.O.C_2H_5$.

Brometone.—Tribromo tertiary butyl alcohol, $CBr_3.C(CH_3)_2OH$.

Brominol.—Brominated sesamé oil (33 % Br).

Brominoleum. See brominol.

Bromochinol.—Acid dibromosalicylate of quinine, $C_{20}H_{24}N_2O_2,2C_6H_2Br_2(OH)COOH$.

Bromoglidin.—Wheat gluten preparation containing 10 % Br.

Bromogluten.—Vegetable albumin preparation containing 8 % Br.

Bromolein.—Brominated unsaturated fatty acids of almond oil (20 % Br).

Bromoprotein. See bromogluten.

Bromotan.—Bromotannin-methylene-urea.

Bromural.—*α*-Bromoisovalerylurea, $C_4H_8Br.CO.NH.CO.NH_2$.

Brophenin.—Bromoisovalerylphenocoll; a brominated phenetidine derivative.

Brovalol.—Bornyl bromovalerate, $C_4H_8Br.COO.C_{10}H_{17}$.

Bynin.—Liquid malt extract.

Cacodyliagol.—Guaiacol cacodylate, $(CH_3)_2AsO.O.C_6H_4(OCH_3),H_2O$.

Cajuputol.—Cineol (eucalyptol), $C_{10}H_{18}O$.

Calcidine.—Calcium iodide.

Calcinol.—Calcium iodate.

Calcusol.—Effervescent preparation of potassium bicarbonate and piperidine-*p*-sulphamine benzoate, $SO_2(NH_2)C_6H_4COOH,C_5H_{11}N$.

Calomelol.—Colloidal calomel.

Camphoid.—Collodion substitute; 1 part of pyroxylin in 20 parts each of camphor and absolute alcohol, by weight.

Camphoral.—Camphoric acid ester of santalol, $C_8H_{14}(COO)_2(C_{15}H_{23})_2$.

Camphosan.—Solution of 15 parts of camphoric acid methyl ester in 85 parts of santalol.

Canadol.—Light petroleum spirit, sp. gr. 0.650-0.700.

Casumen.—Soluble form of casein ("flocculent casein"); contains 90 % of protein.

Celloidin.—Pyroxylin purified by solution in alcohol and ether.

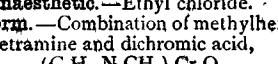
Cellotropin.—Benzoic ester of arbutin, $C_6H_4OC_6H_{11}O_5.O.COC_6H_5$.

Ceredine.—Special dry powdered yeast.

Cerolin.—Solid extract of yeast, containing fat.

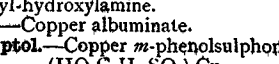
Cetiacol.—Pyrocatechol methyl cetyl ether, $C_6H_4(OCH_3)(OC_{16}H_{33})$.

Chinaphenin. See quinaphenin.
Chinaphthol. See quinaphthol.
Chineonal. See quineonal.
Chininum lygosinatum. See quinine lygosinate.
Chinoform. See quinoform.
Chinosol. See quinosol.
Chloralamid.—Chloral formamide, $CCl_3.CH(OH).CO.NH_2$.
Chloretone.—Trichloro tertiary butyl alcohol, $CCl_3.(CH_3)_2C.OH,\frac{1}{2}H_2O$.
Chlorin.—Dinitroresorcinol, $(NOH)O:C_6H_2:O(NOH)$.
Chlorobrom.—A solution of potassium bromide 6, chloral formamide 6, and water 58 parts.
Chloryl anaesthetic.—Ethyl chloride.
Chromoform.—Combination of methylhexamethylenetetramine and dichromic acid, $(C_6H_{12}N_4CH_3)_2Cr_2O_7$.
Chrysoform.—Dibromodi-iodohexamethylenetetramine, $C_6H_8Br_2I_2N_4$.
Cibrola.—Preparation of milk and glycerophosphates.
Cicatricine.—A solution containing thiosinamine 20, antipyrine 33, and eucaine lactate 0.65 part per 100.
Citarin.—Sodium anhydromethylenecitrate,

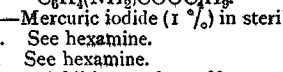


Citrocoll.—Neutral aminophenacetin citrate.
Cocaethylin.—Ethyl ester of benzoylecgonine, $C_6H_5CO.C_8H_{13}NO.COOC_2H_5$.
Codeonal.—Mixture of 1 part of medinal and 2 of codeine-veronal.
Colalin.—Cholalic acid, $C_{24}H_{40}O_5,H_2O$.
Coryfin.—Menthyl ethyl glycollate, $CH_2O(C_{10}H_{19}).COOC_2H_5$.
Coxpyrin. See acetosal.
Cresegol.—Mercury-potassium salt of cresolsulphonic acid.
Cresosteril.—Acid ortho-oxalic ester of *m*-cresol, $CH_3.C_6H_4O.C(OH)_2.C(OH)_2.OC_6H_4(CH_3)$.
Cryogenin.—*m*-Benzaminosemicarbazide, $NH_2.CO.C_6H_4NH.NH.CO.NH_2$.
Cupferron.—Ammonium compound of nitrosophenyl-hydroxylamine.
Cupratin.—Copper albuminate.
Cupri-aseptol.—Copper *m*-phenolsulphonate, $(HO.C_6H_4.SO_3)_2Cu$.
Cupricin.—Cuprous cyanide.
Cuprocitrol.—Copper citrate, $2Cu_2C_6H_4O_7,5H_2O$.
Cuprol.—Compound of nucleinic acid and copper.
Cusylol.—Soluble copper citrate.
Cycloform.—Isobutyl ester of *p*-aminobenzoic acid, $C_6H_4(NH_2)COOC_4H_9$.
Cypridol.—Mercuric iodide (1 %) in sterilised oil.
Cystamin. See hexamine.
Cystogen. See hexamine.
Cystopurin.—Addition product of hexamethylenetetramine and sodium acetate, $C_6H_{12}N_4,2C_2H_3O_2Na,6H_2O$.

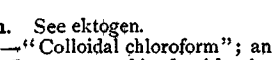
Deba. See veronal.
Dentalone.—Solution of chloretone in essential oils.
Dermogen. See ektogen.
Desalgin.—"Colloidal chloroform"; an albuminous substance combined with about 25 % $CHCl_3$.
Dial-Ciba.—Diallylbarbituric acid,



Diaspirin.—Succinylsalicylic acid, $(CH_2.COO)_2(C_6H_4COOH)_2$.
Digipotene.—Preparation containing the whole of the glucosides of digitalis leaves.
Dioform.—Acetylene dichloride, CHCl:CHCl.
Diogen.—Sodium salt of aminonaphtholdisulphonic acid, $NH_2.C_{10}H_4(OH)(SO_3Na)_2$.
Diogenal.—Dibromopropyldiethylbarbituric acid,



Dioxogen.—A 30 % solution of hydrogen peroxide.
Diplosal.—Salicylosalicylic acid, $HO.C_6H_4.CO.O.C_6H_4.COOH$.
Dipropœsin.—Urea derivative containing the residues of 2 mols. of propæsin, $CO(NH.C_6H_4.CO_2C_3H_7)_2$.
Disalol.—Phenyl salicylosalicylate, $HO.C_6H_4.CO.O.C_6H_4.COOC_6H_5$.
Dispermin.—Piperazine,



Durine.—A formalin preparation.
Dymal.—Didymium salicylate.
Edinol.—*m*-Amino-*o*-hydroxybenzylalcohol hydrochloride, $HO.C_6H_3(NH_2)CH_2OH,HCl$.
Ehrlich-Hata "606." See salvarsan.
Ektogen.—Zinc peroxide.
Elarson.—Strontium salt of chloroarsenobehenolic acid (13 % As.).
Elbon.—Cinnamoyl-*p*-hydroxyphenylurea.
Electrargol.—Electrolytic colloidal silver.
Embarin.—Sodium mercurisalicylsulphonate.
Empyroform.—Condensation product of tar and formaldehyde.
Enesol.—Mercury salicylarsenate (38 % Hg).
Epinene.—3.4-Dihydroxyphenylethylmethylamine, $(HO)_2C_6H_3.CH_2.CH_2.NH.CH_3$.
Epinephrine.—*o*-Dihydroxy-4-methylaminoethanolbenzene, $(HO)_2.C_6H_3.CH(OH).CH_2.NH.CH_3$.
Episine.—1-Methyl-4.5-diphenyleneimidazole,

Epirenan. See adrenaline.
Erepton.—Meat preparation in which proteins are completely resolved into amino-acids.
Ericin. See mesotan.
Ervasin.—Acetylcresotinic acid.
Escalin.—Aluminium powder mixed to a paste with glycerin.
Estoral.—Menthyl borate, $B(O.C_{10}H_{19})_3$.
Euboruyl.—α-Bromoisovaleric ester of borneol, $C_4H_8Br.COOC_{10}H_{17}$.
Eucodeine.—Codeine methyl bromide, $C_{18}H_{21}NO_3,CH_3Br$.
Eucol.—Guaiacol acetate, $CH_3O.C_6H_4O.C_2H_3O$.
Eudrenine.—A solution containing 0.01 grm. of eucaine and 0.03 mgrm. of adrenaline per c.c.
Euguform.—Acetylated guaiaform (condensation product of guaiacol and formaldehyde).
Eulatin.—Mixture of *p*-bromobenzoic acid, *o*-aminobenzoic acid, and antipyrine.
Eumydrine.—Methylatropine nitrate, $C_{16}H_{20}NO_3(CH_3)_2NO_3$.
Euphyllin.—Mixture of equal proportions of primary and secondary theophylline-ethylenediamine, $C_2H_4(NH_2)_2,C_7H_8N_4O_2 + C_2H_4(NH_2)_2,2C_7H_8N_4O_2$
Eupnine.—Caffeine preparation containing iodine.
Euporphine.—Apomorphine methyl bromide, $C_{17}H_{17}NO_2.CH_3Br,H_2O$.

Eupyrine.—*p*-Phenetidine-vanillin ethyl carbonate, $C_6H_4(OC_2H_5)N:CH.C_6H_3(OCH_3)O.CO_2C_2H_5$.

Euresol.—Resorcinol monoacetate, $C_6H_5(OH)(O.C_2H_3O)$.

Euquinine.—Quinine ethyl carbonate, $C_2H_5O.CO.OC_{20}H_{23}N_2O$.

Euscopol.—Inactive scopolamine hydrobromide, $C_{17}H_{21}NO_4,HBr$.

Eustenin.—Addition product of theobromine-sodium and sodium-iodide, $C_7H_7N_4O_2Na,NaI$.

Exodin.—Mixture of diacetylrufigallic acid tetramethyl ether 23, rufigallic hexamethyl ether 30, and acetylrufigallic pentamethyl ether 47 %.

Fæxin. See ceredine.

Fermenlactyl.—Preparation of lactic acid bacilli.

Feronuclin.—Dry yeast extract.

Ferratogen. See ferrinol.

Ferrichthol.—Ichthyol preparation containing iron.

Ferrinol.—Iron nucleinate; contains 21 % Fe_2O_3 and 2½ % P.

Fibrolysin.—15 % solution of a combination of thiosinamine (2 mols.) and sodium salicylate (1 mol.).

Fluoram.—Ammonium bifluoride.

Forgenin.—Tetramethyl-ammonium formate, $H.COON(CH_2)_4$.

Formamint.—Preparation obtained from 1 mol. of lactose and at least 5 mols. of formaldehyde.

Forman.—Chloromethyl menthyl ether, $C_{10}H_{19}O.CH_2Cl$.

Formicin.—Formaldehyde-acetamide, $CH_3.CO.NH.CH_2OH$ or $CH_3.C(:NH).O.CH_2OH$.

Formidin.—Methylenedisalicylic iodide, $C_{15}H_{16}O_6I_2$.

Formitrol.—Formaldehyde preparation.

Formolyptol. See formitrol.

Formurol.—Addition product of hexamethylenetetramine and sodium citrate, $C_6H_{12}N_4,C_6H_7O_7Na$.

Fredo.—Calcium hydrosulphite.

Furfurin.—A glyoxaline derivative, $C_3H_3N_2(C_4H_3O)_3$.

Gaduol.—Extract containing the alcohol-soluble constituents of cod-liver oil.

Gallogen.—Ellagic acid, $C_{14}H_6O_8$.

Gastrosan.—Bismuth basilicylate.

Gaultheriasalol.—Methyl salicylosalicylate, $HO.C_6H_4.CO.OC_6H_4.COOCH_3$.

Glidine.—A protein preparation from wheat.

Glonoin.—Nitroglycerin.

Glycarbin.—Glyceryl carbonate.

Glycerin-formal.—A condensation product of formaldehyde and glycerol, $O.CH_2.O.CH_2OH.CH{-\!\!-\!\!-}CH_2$.

Glycobrom.—Glyceryl ester of dibromohydrocinnamic acid, $C_3H_5[O.CO.(CHBr)_2C_6H]_3$.

Glycocyamine.—Guanidine acetic acid.

Glycosal—Monosalicylic ester of glycerol, $C_3H_5(OH)_2.O.CO.C_6H_4(OH)$.

Gomaine.—Solution of iodoform and camphor in sesamé oil.

Griserin, Novum.—Iodohydroxyquinoline sulphonic acid, $C_9H_4I(OH)(SO_3H)N$, mixed with 20 % $NaHCO_3$.

Guaiachinol.—Quinine dibromoguaiacolate, $C_6H_2Br_2(OCH_3)OH,C_{20}H_{24}N_2O_2$.

Guaiamaltin.—Mixture of malt extract and potassium sulphoguaiacolate.

Guatannin.—Guaiacol tannocinnamate.

Gynoval.—Isobornyl isovalerate, $C_4H_9.COOC_{10}H_{17}$.

Hectine.—Sodium benzosulpho-*p*-aminophenylarsinate, $C_6H_5.SO_2NH.C_6H_4.AsO(OH)(ONa)$.

Hediorite.—Lactone of α-glucoheptonic acid.

Hegonon.—Ammonio-silver nitrate-albumose (7 % Ag).

Helcosol.—Basic bismuth pyrogallate, $HO.C_6H_3O_2BiOH$.

Helicon. See acetosal.

Helmitol.—Hexamethylenetetramine anhydromethylenecitrate, $C_6H_{12}N_4,C_7H_6O_7$.

Hemisine. See adrenaline.

Hermophenyl.—Mercury sodium phenoldisulphonate, $(SO_3Na)_2C_6H_2O(Hg)$.

Hetoform.—Basic bismuth cinnamate, $(C_6H_5.CH:CH.CO_2)_3Bi,Bi_2O_3$.

Hetralin.—Addition product of resorcinol and hexamethylenetetramine, $C_6H_{12}N_4,C_6H_4(OH)_2$.

Hexal.—Hexamethylenetetramine salicylsulphonic acid, $C_6H_{12}N_4,(HO)C_6H_3(COOH)SO_3H$.

Hexamine.—Hexamethylenetetramine, $C_6H_{12}N_4$.

Hexanatrin.—Combination of hexamethylenetetramine and acid sodium phosphate.

Hexanitrin.—Mannitol hexanitrate, $CH_2O(NO_2)(CHO.NO_2)_4.CH_2ONO_2$.

Histamin.—β-Iminazolylethylamine.

Homorenon.—Ethylaminoacetopyrocatechol hydrochloride, $(HO)_2.C_6H_3.CO.CH_2.NH(C_2H_5),HCl$.

Hopogan. See magnesium perhydrol.

Hydramin.—A combination of *p*-phenylenediamine and quinol.

Hydrargol.—Mercury succinimide, $[C_2H_4(CO)_2N]_2Hg$.

Hydrargotin.—Mercury tannate (50 %] Hg).

Hydrarsan.—Solution of a mixture of arsenious, mercuric, and potassium iodides and antipyrine.

Hydriodol. See cypridol.

Hydropyrin. See apyron.

Hydrosulphite N.F.—Condensation product of formaldehyde and sodium hydrosulphite; a mixture of formaldehyde sodium bisulphite, $NaHSO_3,CH_2O$, and formaldehyde-sodium sulphoxylate, $NaHSO_2,CH_2O$.

Hydrosulphite N.F. extra, or conc., or extra conc.—Formaldehyde-sodium-sulphoxylate.

Hyperol.—Compound of hydrogen peroxide and urea, with a trace of citric acid to render it stable.

Hypnogen. See veronal.

Hydraldite A. See hydrosulphite N.F.

Hydraldite C. See hydrosulphite N.F. extra.

Iachiol.—Silver fluoride.

Ichthargan.—Silver ichthyolsulphonate (30 % Ag).

Ichthermol.—Mercury compound of ichthyol.

Ichthosulphol.—Ichthyol.

Ichthynal. See ichthosulphol.

Ichthyolidin.—Piperazine ichthyolate.

Ichthyol-salicyl.—Mixture of ichthyol and sodium salicylate.

Imogen.—Sodium diaminonaphtholsulphonate, $(NH_2)_2C_{10}H_5(OH)SO_3Na$.

Indoform.—Salicylic methylene acetate; from formaldehyde and acetylsalicylic acid.

Insipin.—Diglycollic ester of quinine sulphate, $(CH_2COO.C_{20}H_{23}N_2O)_2O,H_2SO_4,3H_2O$.

Iodanytol.—10 % solution of iodine in anytin (a 33 % solution of ichthyol).

Iodeigon.—Albumin preparation containing iodine.

Iodin.—Iodised arachis oil.

Iodinol.—Iodised sesamé oil.

Iodival.—Monoiodoisovalerylurea, $(CH_3)_2CH.CHI.CO.NH.CO.NH_2$.

Iodocol.—Prepared from guaiacol and iodine in sodium iodine.

Iodofan.—Monoiododihydroxybenzene-formaldehyde.

Iodoglidine.—Preparation of wheat gluten containing 10 % I.

Iodogtobin.—Di-iodotyrosine, $HO.C_6H_2I_2.CH_2.CH(COOH)NH_2$.

Iodogluten.—Preparation of vegetable albumin containing 8 % I.

Iodolen.—Combination of iodol (tetra-iodopyrrole) and albumin; contains 30 % idol.

Iodolin.—Quinoline chloromethyliodochloride, $C_9H_7N(CH_2Cl)ClI$.

Iodolinum. See iodolin.

Iodolysin.—Preparation similar to iodine; contains 43 % thiosinamine and 47 % I.

Iodomenim.—Iodised casein containing bismuth (10 % I).

Iodophenin.—Tri-iodophenacetin.

Iodoprotein.—Albumin preparation containing 10 % I.

Iodozol.—Di-iodo-*p*-phenolsulphonic acid, $C_6H_2I_2(OH)SO_3H,3H_2O$.

Iodylin.—Bismuth iodosalicylate.

Iodyloform.—Iodised gelatin (10 % I).

Iohydrin.—Di-iodoisopropyl alcohol, $CH_2I.CH(OH).CH_2I$.

Iothion. See iohydrin.

Isarol.—See ichthosulphol.

Isoform.—*p*-Iodoxyanisol, $CH_3O.C_6H_4.IO_2$.

Isopral.—Trichloroisopropyl alcohol, $CCl_3.CH(OH).CH_3$.

Istizin.—1.8-Dihydroxyanthraquinone.

Jecovol.—Emulsion of cod-liver oil with glycerophosphates of sodium, calcium, and iron.

Johá.—Solution of 40 % of salvarsan in iodinol.

Kachin.—A pyrocatechol photographic developer.

Kakodyljacol. See cacodyliagol.

Kalmopyrin.—Calcium acetylsalicylate, $(C_2H_3O.OC_6H_4.COO)_2Ca$.

Kalzose.—Casein preparation containing calcium.

Kephaldol.—Preparation made from phenetidine and salicylic and citric acids.

Kinetine.—Combination of quinine and hectine.

Kineurine.—Quinine glycerophosphate, $C_3H_7O_3H_2PO_3(C_{20}H_{24}N_2O_2)_2,4H_2O$.

Koronium bromide.—Strontium bromide, $SrBr_2,6H_2O$.

Krelos.—Mixture of tar distillates and rosin soap solution.

Kresegol. See cresegol.

Kresosteril. See cresosteril.

Kryogenin. See cryogenin.

Kynurin.—*p*-Hydroxyquinoline, $C_9H_6(OH)N$.

Lactagol.—Powdered extract of cotton-seed.

Lactanin.—Bismuth bilacto-monotannate.

Lacteol.—Preparation of lactic acid bacilli.

Lactigen. See lacteol.

Lactilloids. See lacteol.

Lactobacciliine. See lacteol.

Lactone. See lacteol.

Laxans. See purgen.

Laxatol. See purgen.

Laxen. See purgen.

Laxoin. See purgen.

Lecithol.—Lecithin from egg yolk.

Lecutyl.—Combination of lecithin and copper cinnamate (1·5 % Cu).

Lenicet.—Basic aluminium acetate, $Al'_2(OH)_2(C_2H_3O_2)_4,H_2O$.

Lentin.—*m*-Phenylenediamine hydrochloride, $C_6H_4(NH_2)_2,2HCl$.

Leptynol.—Colloidal palladous hydroxide suspended in sesamé oil.

Leucoline.—Quinoline, $C_6H_4\begin{matrix}CH:CH\\N:CH\end{matrix}$

Levurargyre.—Mercury compound of nucleoprotein.

Levuretin.—Dried yeast cells.

Levurinose. See levuretin.

Lipobromol.—Brominated poppyseed oil (33 % Br).

Lipoiodin.—Di-iodobrassidic acid ethyl ester, $C_{19}H_{39}CI:CI.CO_2C_2H_5$.

Lithium-diuretin.—Addition product of theobrominelithium and lithiumsalicylate, $C_7H_7N_4O_2Li,HO.C_6H_4.CO_2Li$.

Litthyol. See ichthosulphol.

Lodal.—An oxidation product of laudanosine.

Lofotol.—Cod-liver oil charged with carbon dioxide.

Lucidol.—Benzoyl peroxide $(C_6H_5.COO)_2O_2$.

Luesan.—Glidine preparation containing mercury.

Luminal.—Phenyl ethyl malonylurea,

$$\begin{matrix}C_2H_5\\C_6H_5\end{matrix}\!\!>\!C\!<\!\begin{matrix}CO.NH\\CO.NH\end{matrix}\!\!>\!CO$$

Lycin. See acidol.

Lygosin.—Di-hydroxydibenzalacetone, $HO.C_6H_4.CH:CH)_2CO$.

Lysochlor. Chloro-*m*-cresol, $C_6H_3Cl(CH_3)OH$.

Lysoform.—A liquid formaldehyde potassium soap.

Magnesium-perhydrol.—Mixture containing magnesia and 15 or 25 % MgO_2.

Malonal. See veronal.

Malourea. See veronal.

Maltyl.—Dry malt extract; contains about 90 % of soluble carbohydrates.

Maretin.—*m*-Tolylsemicarbazide, $CH_3.C_6H_4.NH.NH.CO.NH_2$.

Maricol.—Magnesium ricinoleate, $(HO.C_{17}H_{32}CO_2)_2Mg$.

Medinal.—Sodium compound of veronal.

Melrubin.—Sodium 1-phenyl-2.3-dimethylpyrazolone-4-aminomethane sulphonate, $C_{11}H_{11}N_2O.NH.CH_2.SO_3Na$.

Melubrin.—Mercury salicylsulphonate.

Menthophenol.—Mixture of phenol 1, menthol 3 parts.

Mercuriocoleolo.—Double oleate of cholesterol and mercury.

Mergal.—A combination of mercury cholate and albumin tannate.

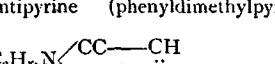
Merjodin.—Mercury di-iodophenol-*p*-sulphonate, $(HO.C_6H_2I_2.SO_3)_2Hg$.

Merlusan.—Mercury compound of tyrosine (53 % Hg), $C_9H_9O_2NHg$.

Merochinal.—Mercury hydroxyquinolinesulphonate, $(HO.C_6H_5N.SO_3)_2Hg$.

Mesotan.—Salicylic methoxymethyl ester, $HO.C_6H_4.COO.CH_2.OCH_3$.

Methozin.—Antipyrine (phenyldimethylpyrazolone,



Methylrhodin.—Methyl acetylsalicylate, $C_2H_3O.O.C_6H_4.CO_2CH_3$.

Metoquinone.—Addition product of metol (methyl-*p*-aminophenol) and quinol, $C_6H_4[HO(CH_3)NH.C_6H_4.OH]_2$.

Metramine. See hexamine.

Migralgine.—Mixture of antipyrine 88, caffeine 9, and salycylic acid 3 parts, fused together.

Momordicine.—Elaterin, $C_{29}H_{28}O_5$.

Monotal.—Guaiacol methyl glycollate, $CH_2(OCH_3).COOC_6H_4.OCH_3$.

Morphosan.—Morphine methyl bromide, $C_{17}H_{19}O_3N.CH_3Br,H_2O$.

Mucogeene.—An anthraquinone derivative, $C_{18}H_{15}N_2O_2Cl$.

Mydriasine.—Atropine methyl bromide, $C_{17}H_{23}NO_3,CH_3Br$.

Naphtholsalol.—*β*-Naphthyl salicylate, $HO.C_6H_4.COO.C_{10}H_7$.

Narcyl.—Ethylmarceine hydrochloride, $C_{23}H_{26}(C_2H_5)NO_3,HCl$.

Nargol.—Silver nucleinate (10 % Ag).

Nealpon. See pantopon.

Neoform.—Bismuth compound of tri-iodophenol, $C_6H_2I_3OBi(OH)_2,Bi_2O_3$.

Neoleptol.—Triformyltrimethylenetriamine.

Neopine.—Hydroxycodeine, $C_{18}H_{20}NO_3(OH)$.

Neopyrin.—Valerylaminoantipyrine.

Neosalvarsan.—Sodium 3.3'-diamino-4.4'-dihydroxy-arsenobenzene-formaldehyde sulphoxylate, $NH_2.C_6H_3(OH)As.As.C_6H_3(OH)NH(CH_2O)SONa$.

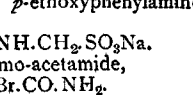
Neosiode.—Iodocatechin $(C_{15}H_{14}O_6,3H_2O)_2I$.

Nerolin.—*β*-Naphthyl methyl ether, $C_{10}H_7O.CH_3$.

Neuraltein.—Sodium *p*-ethoxyphenylaminomethane sulphonate, $C_2H_5O.C_6H_4.NH.CH_2.SO_3Na$.

Neuronal.—Diethylbromo-acetamide, $(C_2H_5)_2CBr.CO.NH_2$.

Nitron.—1.4-Diphenyl-3.5-endanilodihydrotriazole,



Nizin.—Zinc sulphanilate, $(NH_2.C_6H_4.SO_3)_2Zn$.

Novargan.—Protein preparation containing 10 % Ag.

Novaspirin.—Methylenecitrylsalicylic acid.

Novatophan.—Ethyl 6-methyl-2-phenylquinoline-4-carboxylate, $C_6H_5.C_9H_4N(CH_3)COOC_2H_5$.

Noviform.—Bismuth compound of tetrabromopyrocatechol.

Novocaine.—*p*-Aminobenzoyldiethylaminoethanol hydrochloride, $NH_2.C_6H_4CO.O.CH_2.CH_2.N(C_2H_5)_2,HCl$.

Novocol.—Sodium monoguaiacol phosphate.

Nucleogen.—Preparation containing iron nucleinate and arsenic.

Oleanodyne.—Preparation containing oleic acid, aconitine, atrophine, morphine, and veratrine.

Oleoguaiacol.—Guaiacol oleate, $CH_3O,C_6H_4O.CO.C_{17}H_{33}$.

Omnopon. See pantopon.

Omorol. See novargan.

Optochin.—Ethylhydrocupreine.

Orexin.—Phenyldihydroquinazoline.

Orsudan.—Sodium methyl acetyl-*p*-aminophenylarsinate, $C_2H_3O.NH.C_6H_3(CH_3).AsO(OH)(ONa)$.

Ortizon. See hyperol.

Ovoferrin.—Vitellin preparation containing iron.

Oxylith.—Sodium peroxide.

Oxyntin.—A combination of albumin and hydrochloric acid.

Palmiacol. See cetiacol.

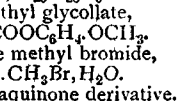
Pantopon.—Mixture of the soluble hydrochlorides of opium alkaloids.

Parabismut.—Bismuth paranucleinate.

Paracodine.—Dihydrocodeine, $C_{17}H_{19}(OCH_3)(OH)NO$.

Paralysol.—Solid cresol preparation, $C_6H_4(CH_3)OK,3C_6H_4(CH_3)OH$.

Paraxin.—Dimethylamino-1.7-dimethylxanthine.



Pegnine.—Preparation of lactose and rennet.

Pellidol.—Diacetylaminoazotoluene.

Pepsalia.—Preparation of pepsin and sodium chloride.

Perborax.—Sodium perborate, $NaBO_3,4H_2O$.

Perborol. See perborax.

Perhydrit. See hyperol.

Perhydrol.—Solution of hydrogen peroxide, 100 vol., or 30 % by weight.

Permidan.—Dimethylaminopyrazolone, $C_5H_9N_3O$.

Phenalgin.—Phosphoammonioaccetanilide.

Phenamine.—Amino-acet-*p*-phenetidine hydrochloride, $C_2H_5O.C_6H_4.NH.CO.CH_2.NH_2,HCl$.

Phenolax. See purgen.

Phenosal.—Monophenetidide of salicylacetic acid, $COOH.C_6H_4.O.CH_2.CO.NH.C_6H_4.OC_2H_5$.

Phenoval.—Bromovalerylphenetidine, $C_4H_8Br.CO.NH.C_6H_4.OC_2H_5$.

Phenyform.—Condensation product of phenol and formaldehyde.

Phenylon. See methozin.

Phobrol.—50 % solution of chloro-*m*-cresol in potash castor oil soap.

Photoxylin. See celloidin.

Picrastol.—Dimethyloldiformylmethenyltetramethylenepentamine, $C_9H_{17}N_5O_4$.

Picratol.—Silver picrate.

Pinakol.—A pyrogallol photographic developer in which part of the alkali usually employed is replaced by sodium aminoacetate.

Piral.—Pyrogallol, $C_6H_3(OH)_3$.

Plecavol.—Consists chiefly of *p*-aminobenzoyleugenol, $NH_2.C_6H_4CO.O.C_6H_3(C_3H_5)OCH_3$, tricresol (a mixture of the three cresols), and formaldehyde.

Pleistopon.—Similar to pantopon, except that it contains no narcotine.

Pneumin.—Condensation product of creosote and formaldehyde.

Pneumosan.—Amyl thiotrimethylamine.

Propæsin.—Propyl ester of *p*-aminobenzoic acid, $NH_2.C_6H_4.COOC_3H_7$.

Proponal.—Dipropylbarbituric acid, $(C_3H_7)_2C\langle{CO.NH \atop CO.NH}\rangle CO$

Proposote.—Creosote phenylpropionate.

Protosal.—Salicyclic acid glycerol formal ester, $HO.C_6H_4.CO.O.CH_2.\underset{\displaystyle O}{CH}-CH_2$.

Protylin.—Albumin preparation containing phosphorus.

Purgatin.—Anthrapurpurin diacetate, $C_{14}H_5O_2(OH)(O.C_2H_3O)_2$.

Purgatol. See purgatin.

Purgen.—Phenolphthalein, $C_6H_4\langle{C(C_6H_4.OH)_2 \atop OC}\rangle O$.

Pyoktanin.—Methyl violet, $[C_6H_4.N(CH_3)_2]_2(C_6H_4.NH.CH_3)C.Cl$.

Pyracetosalyl.—Addition product of antipyrine and acetylsalicylic acid, $C_{11}H_{12}N_2O + C_2H_3O.OC_6H_4.COOH$.

Pyrobromone.—Bromodimethylaminoantipyrine.

Pyronal.—Antipyrine salicylacetate, $C_{11}H_{12}N_2O, HO.C_6H_4CO.CH_2.COOH$.

Pyrophan.—Combination of pyrogallol and dimethylamine.

Quietol.—Dimethylaminodimethylisovalerylpropyl ester hydrobromide.

Quinaphenin.—Phenetidine quinine carbonic ester, $CO(NH.C_6H_4.OC_2H_5)(C_{20}H_{23}N_2O_2)$.

Quinaphthol.—Quinine β-naphtholsulphonate, $C_{20}H_{24}N_2O_2,(HO.C_{10}H_6.SO_3H)_2$.

Quineonal.—Compound of quinine and veronal.

Quinine lygosinate.—Dihydroxydibenzalacetone-quinine, $CO(CH:CH.C_6H_4OH.C_{20}H_{24}N_2O_2)_2$.

Quinoform.—Quinine formate, $C_{20}H_{24}N_2O_2$, $HCOOH$; also a condensation product of cinchotannic acid and formaldehyde.

Quinopyrin.—A combination of antipyrine, 2, and quinine hydrochloride, 3 parts.

Quinosol.—Mixture of hydroxyquinoline and potassium sulphates, $C_9H_6NOSO_3K,4H_2O$.

Quinotropin.—Hexamethylenetetramine quinate, $C_6H_{12}N_4,C_6H_7(OH)_4CO_2H$.

Regulin,—Broken-up agar-agar with 25 % of Cascara-extract.

Resaldol.—Resorcylbenzoic acid ethyl ester, $(HO)_2C_6H_3.CO.C_6H_4.CO_2C_2H_5$.

Rexotan.—Methylenhtannin-urea, $C_{14}H_9O_9.CH_2.NH.CO.NH_2$.

Rheumatin.—Saloquinine salicylate, $HO.C_6H_4.COO.C_{20}H_{23}N_2O,C_6H_4(OH)COOH$.

Rhodaform.—Addition product of hexamethylenetetramine and methyl thiocyanate, $C_6H_{12}N_4,CH_3CNS$.

Riopan.—Soluble brown powder containing 50 % of ipecacuanha alkaloids in the form of their hydrochlorides.

Rongalite C. See hydrosulphite N.F. extra.

Sabromine.—Calcium dibromobehenate (29 % Br), $(C_{22}H_{41}O_2Br_2)_2Ca$.

Sajodin.—Calcium monoiodobehenate, $(C_{22}H_{42}O_2I)_2Ca$.

Salacetin. See acetosal.

Saletin. See acetosal.

Salibromin,—Dibromosalicylic methyl ester, $C_6H_2Br_2(OH)COOCH_3$.

Salicreol.—Creosote salicylate.

Salimenthol.—Menthyl salicylate, $HO.C_6H_4.COOC_{10}H_{19}$.

Salit.—Bornyl salicylate, $HO.C_6H_4.COO,C_{10}H_{17}$.

Salocreol. See salicreol.

Saloquinine.—Salicylquinine, $HO.C_6H_4.CO_2.C_{20}H_{23}N_2O$.

Salufer.—Sodium silicofluoride.

Salvarsan.—Dihydroxydiaminoarsenobenzene dihydrochloride, $HCl.NH_2(OH)C_6H_3.As.As.C_6H_3(OH)NH_2.HCl,2H_2O$.

Salvarsan, New. See neosalvarsan.

Santheose.—Theobromine, $C_5H_2(CH_3)_2N_4O_2$.

Santyl.—Santalyl salicylate, $HO.C_6H_4.COO.C_{15}H_{23}$.

Sauerin.—Preparation of lactic acid baccilli.

Savore.—Preparation of milk, cereal proteins and albumoses, and carbohydrates.

Scopomorphine.—Sterilised solution containing per c.c., 0·0006 grm. of euscopol and 0·015 grm. of morphine hydrochloride.

Sedeff.—Effervescent preparation containing opium, bismuth, and digestive ferments.

Sennatin.—Preparation containing the active principles of senna leaves.

Sennax.—Preparation containing the water-soluble glucosides of senna leaves.

Sidonal, New.—Mixture of quinic acid, $C_6H_7(OH)_4CO_2H$, and its anhydride.

Soamin.—Sodium arsanilate, $NH_2.C_6H_4.AsO(OH)(ONa),5H_2O$.

Solurol.—Thyminic acid (nucleotinphosphoric acid), $C_{36}H_{46}N_4O_{17}(P_2O_5)_2$.

Somnoform.—Mixture of ethyl chloride 60, methyl chloride 35, and ethyl bromide 5 %.

Sophol.—Silver formonucleinate (20 % Ag).

Spirarsyl.—Sodium salt of arsenophenylglycine, $(CO_2Na.CH_2.NH.C_6H_4)_2As_2$.

Spirosal.—Monoglycol ester of salicylic acid, $HO.C_6H_4.COO.CH_2.CH_2OH$.

Stearosan.—Compound of santalol and stearic acid.

Stovaine.—Hydrochloride of dimethylamino tertiary amyl benzoate, $C_6H_5COO.C(CH_3)(C_2H_5)CH_2N(CH_3)_2,HCl$.

Styptol.—Cotarnine phthalate, $(C_{12}H_{13}NO_3)_2,C_6H_4(COOH)_2$.

Subcutin.—Anæsthesin phenolsulphonate, $C_6H_4(COOC_2H_5)NH_2,HO.C_6H_4.SO_3H$.

Sublamine.—Mercuric ethylenediamine sulphate (43 % Hg).

Sucramine.—Ammonium salt of saccharin.

Sulfoid.—Preparation of colloidal sulphur (80 % S) with an albuminous substance as protective colloid.

Sulphoform.—Triphenylstibine sulphide, $(C_6H_5)_3SbS$.

Suprarenaline. See epinephrine.

Suprarenine. See adrenaline.

Synthalin.—Piperonylquinolinecarboxylic acid methyl ester, $CH_2O_2.C_6H_3.C_9H_5N.COOCH_3$.

Syrgol.—Colloidal silver.

Tachiol.—Silver fluoride.

Tanargan.—A combination of tannin and silver albuminate.

Tanninphenolmethane.—Condensation product of tannin, formaldehyde, and phenol.

Tanninthymolmethane.—Condensation product of tannin, formaldehyde, and thymol.

Tannismuth.—Bismuth bitannate.

Tannisol.—Methyleneditannin $(C_{14}H_9O_9)_2CH_2$.

Tannobromine.—A combination of dibromotannin and formaldehyde.
Tannocreosoform. — Condensation product of tannin, formaldehyde, and creosote.
Tannoguaiaform. — Condensation product of tannin, formaldehyde, and guaiacol.
Tannothymal. See tanninthymolmethane.
Tannyl.—Oxychlorocasein tannate.
Tenosin.—Solution containing, per c.c., 0·0005 grm. of β-iminazolylethylamine and 0·02 grm. of *p*-hydroxyphenylethylamine.
Testijodyl.—Combination of coagulated blood albumin and iodine.
Theobromose. — Lithium compound of theobromine, $C_7H_7N_4O_2Li$.
Theocin.—Sodium compound of theobromine, $C_7H_7N_4O_2Na$.
Theolactin.—Addition product of theobromine-sodium and sodium lactate.
Theosalin.—Addition product of theobromine-sodium and sodium sulphosalicylate, $C_7H_7N_4O_2Na, C_7H_5O_3.SO_3Na$.
Thephorin.—Addition product of theobromine-sodium and sodium formate, $C_7H_7N_4O_2Na, HCO_2Na, H_2O$.
Thermiol.—Sodium phenylpropiolate, $C_6H_5.C : C.CO_2Na$.
Thialion.—Preparation containing sodium sulphate (26 %), citrates of sodium (56), potassium (3) and lithium (3), sodium chloride (3), and water (9 %).
Thigenol.—Sodium salt of ichthoform (condensation product of ichthyol and formaldehyde).
Thiophysem. See tiodine.
Tholaform.—Mixture of equal parts of menthol and trioxymethylene.
Throphleol.—56 % solution of erythrophleine hydrochloride (from casca bark) in eugenol.
Thymatol.—Thymol carbonate, $CO(O.C_{10}H_{12})_2$.
Thymegol.—Mercury potassium salt of thymol-*p*-sulphonate.
Thymolin.—Mixture of naphthalene 18, camphor 1, and thymol 1 part.
Thymoloform.—Condensation product of formaldehyde and thymol.
Thyresol.—Santalol methyl ether, $C_{15}H_{23}O.CH_3$.
Tiodine.—Thiosinamine ethyl iodide, $C_3H_5.NH.CS.NH_2, C_2H_5I$.
Toxynon.—Sodium *m*-acetylaminomercuribenzoate, $HgOH.C_6H_3(NH.C_2H_3O)CO_2Na$.
Tricalcol.—Colloidal combination of tricalcium phosphate and albumin.
Tricarbin. See glycarbin.
Triferrin. See ferrinol.
Trigemin.—Compound of butyl chloral hydrate and pyramidone (dimethylaminoantipyrine).
Trilactine.—Preparation of lactic acid bacilli.
Trinitrin.—Nitroglycerin.
Trixidin.—An emulsion of antimony trioxide (30 % Sb_2O_3).
Tryen. See griserin, novum.
Trygase.—Dried yeast cells.
Trypan Red.—Prepared from tetrazotised benzidinesulphonic acid and 2 mols. of sodium naphthylaminedisulphonate,
$(SO_3H)C_6H_3.N_2.C_{10}H_4(SO_3Na)_2NH_2$
$C_6H_4.N_2.C_{10}H_4(SO_3Na)_2NH_2$.
Tryparosan.—Chlorinated parafuchsin.
Tylcalsin. See kalmopyrin.
Tyllithin. See apyron.
Tylmarin.—Acetyl-*o*-coumaric acid, $C_2H_3O.OC_6H_4.CH : CH.CO_2H$.
Tylnatrin.—Sodium acetylsalicylate, $C_2H_3O.OC_6H_4.COONa$.
Tyramine.—*p*-Hydroxyphenylethylamine hydrochloride, $HO.C_6H_4.C_2H_4.NH_2, HCl$.

Ulmarene. See mesotan.
Unal.—Alkali salt of *p*-aminophenol hydrochloride; *rodinal* is the concentrated solution.
Uraminoantipyrin.—Antipyrylurea, $NH_2CO.NH.C_{11}H_{11}N_2O$.
Urapurgol. See helmitol.
Urea-bromine.—Combination of urea and calcium bromide (36 % Br), $4CO(NH_2)_2, CaBr_2$.
Uritone. See hexamine.
Urocitral.—Addition product of theobromine-sodium and sodium citrate.
Urodonal.—Granular preparation of hexamethylenetetramine, sidonal (piperazine quinate), and lysidine (methylglyoxalidine).
Urogenin.—Additiou product of theobromine and lithium hippurate, $C_7H_8N_4O_2, C_6H_5.CO.NH.CH_2.CO_2Li$.
Urol.—Urea quinate.
Urosin.—Lithium quinate, $C_6H_7(OH)_4COOLi$.
Urotropine, New. See helmitol.

Valamin.—Isovaleric ester of tertiary amyl alcohol.
Valearin.—Valeryltrimethylammonium chloride.
Valisan.—Bornylbromoisovalerate, $C_4H_8BrCO.OC_{10}H_{17}$.
Valyl.—Valeric diethylamide, $C_4H_9.CO.N(C_2H_5)_2$.
Veronal.—Diethylbarbituric acid (diethylmalonylurea),

$$(C_2H_5)_2C\begin{matrix}\diagup CO.NH\\ \diagdown CO.NH\end{matrix}\diagup CO.$$

Veropyrin.—Mixture of dionine (ethylmorphine hydrochloride) 0·01, veronal-sodium 0·2, and kalmopyrin, 0·5 part.
Vesalvine. See hexamine.
Vesipyrine.—Phenyl acetylsalicylate, $CH_3.CO.OC_6H_4.COOC_6H_5$.
Vimopyrin.—*p*-Phenetidine tartrate.
Vioform.—Hydroxyquinoline chloroiodide, $C_9H_6N(OH)ICl$.
Vitafer.—Preparation of milk and glycerophosphates of calcium and sodium.

Xaxa. See acetosal.
Xaxaquin.—Quinine acetylsalicylate, $C_{20}H_{24}N_2O_2, CH_3CO.OC_6H_4.COOH$.

Yara-yara. See nerolin.
Yatren. See griserin, novum.

Zymin.—Special dry powdered yeast.

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